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CHEMISTRY LABORATORY MANUAL BOTTOM
SEDIMENTS

Federal Water Quality Administration
Chicago, Illinois

December 1969

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CHEMISTRY LABORATORY MANUAL
BOTTOM SEDIMENTS

COMPILED BY

GREAT LAKES REGION
COMMITTEE ON ANALYTICAL METHODS

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U.S. Department of Commerce
Springfield, VA. 22151

ENVIRONMENTAL PROTECTION AGENCY
Federal Water Quality Administration

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FOREWORD

Water pollution control agencies during the past two or three years have become concerned over the U. S. Army Corps of Engineers dumping dredgings from shipping channels and harbors into the deep waters of the Great Lakes. The state and federal agencies and the Corps of Engineers recognized the necessity of knowing the chemical content of these dredgings or bottom sediments.

The Corps of Engineers then requested that the Federal Water Pollution Control Administration sample and analyze all bottom sediments in areas to be dredged, prior to dredging. As a result of this request, the Lake Michigan Basin Office developed analytical methods suitable for the analysis of these bottom sediments. It was not long before other FWPCA Basin Offices in the Great Lakes Region requested the Lake Michigan Basin Office's methods. Other Basin Offices soon modified the Lake Michigan Basin Office's methods to suit their particular need.

In October 1967 chemists of several agencies in the Great Lakes Region were requested to develop uniform sampling and analytical methods. A meeting including FWPCA Basin Offices, U. S. Army Corps of Engineers, International Joint Commission and U.S. Lake Survey was held in Cleveland to discuss sampling and analytical methods and establish uniform methods. A committee was appointed to compile a chemistry manual for bottom sediments. The committee consisted of members from all of the above agencies.

After extensive correspondence, exchange of methods among the committee members and several committee meetings, the present manual was compiled.

This manual is being used by all of those agencies mentioned above in the Great Lakes Region and many other federal, state, municipal, consulting firm and university laboratories.

Frederic D. Fuller
Chairman and Editor
Lake Michigan Basin Office

ACKNOWLEDGMENTS

Various tests as given in Standard Methods for the Examination of Water and Wastewater have been modified to better suit Great Lakes Region's objectives and needs. In some instances, new methods have been devised as superior to those in Standard Methods.

For these endeavors by members of the many laboratories in the Great Lakes Region, full credit is given.

Original Methods

Total Ferrous Iron, by C. Ross and C. Potos,
Lake Erie Basin Office

Pesticides, by W. D. Johnson and G. Frye
Lake Michigan Basin Office

Chromium by Polarography, by R. S. Whitworth and E. T. King
Lake Michigan Basin Office

Modified Methods

Toxic Metals, including preparation of sample and methods
for Cu, Cd, Ni, Zn, Pb, Cr, Al, and Mn, by E. T. King,
R. S. Whitworth and S. Zarbin
Lake Michigan Basin Office

Cyanide, by E. T. King, Lake Michigan Basin Office

Sulfide, by E. T. King and S. Zarbin, Lake Michigan Basin Office

Total Phosphorus and Total Soluble Phosphorus, by F. D. Fuller,
R. H. Hall, and M. Huston, Lake Michigan Basin Office

Silica and Manganese, by A. C. Smith, Lake Erie Basin Office

Total Iron, by R. S. Whitworth, Lake Michigan Basin Office

In addition to those chemists mentioned above, credit is given to all chemists in the region for their contributions of thoughts and suggestions.

INTRODUCTION TO
BOTTOM SEDIMENT ANALYSIS

1

1. General Discussion

Bottom sediment analysis gives information as to the chemical and biochemical characteristics of the overlying water mass and the immediate underlying sediment itself.

The productivity of a stream or lake is reflected in the chemical composition of the bottom sediments.

Comprehensive bottom studies show potential polluttional loadings of toxic materials, nutrients, and organic substance.

2. Sampling

2.1 Bottom sediment samples are collected with a Petersen or Shipek dredge lowered slowly in order to cause the least possible disturbance to the surface sediment (water-sediment interface). A satisfactory core sampler would be more desirable.

2.2 When hopper dredging is employed, inflow grab samples are taken from two forward and two aft inflow chutes over an eight hour period and composited. The composite is thoroughly mixed and samples withdrawn. Overflow samples are collected at four overflow weir locations and composited in the same manner. Sampling from the hopper itself is accomplished by allowing a 20-quart bucket to remain in the bottom of the hopper at four locations for five minutes and compositing these grabs similar to the inflow and outflow samples.

2.3 When bucket dredging is used, five samples from each compartment would be taken after the barge is filled. A one-inch diameter aluminum tube, ten feet long will be used to take samples. One composite is made for each barge and two barges per week.

2.4 When hydraulic dredging is employed, grab samples are taken from the discharge pipe and composited. The sample is taken from the well-mixed composite.

3. Preservation and Storage

All samples should be well iced and no preservative added. If the samples can not be analyzed the day they are collected, they should be frozen as soon as possible. Sample containers should be filled only three-fourths full to prevent breaking, when frozen.

4. Preliminary Preparation of Bottom Sediment Samples

The sample is passed through a 2 mm (approximately 10 mesh) sieve by rubbing with a rubber stopper, if necessary. This removes large pieces of foreign material such as stones and twigs.

The sieved sample is blended to a homogeneous mixture in a blender for 2 minutes at high speed. The sample is now ready for analysis.

SCHEMATIC ANALYSIS OF SEDIMENT

E_p and pH performed in field

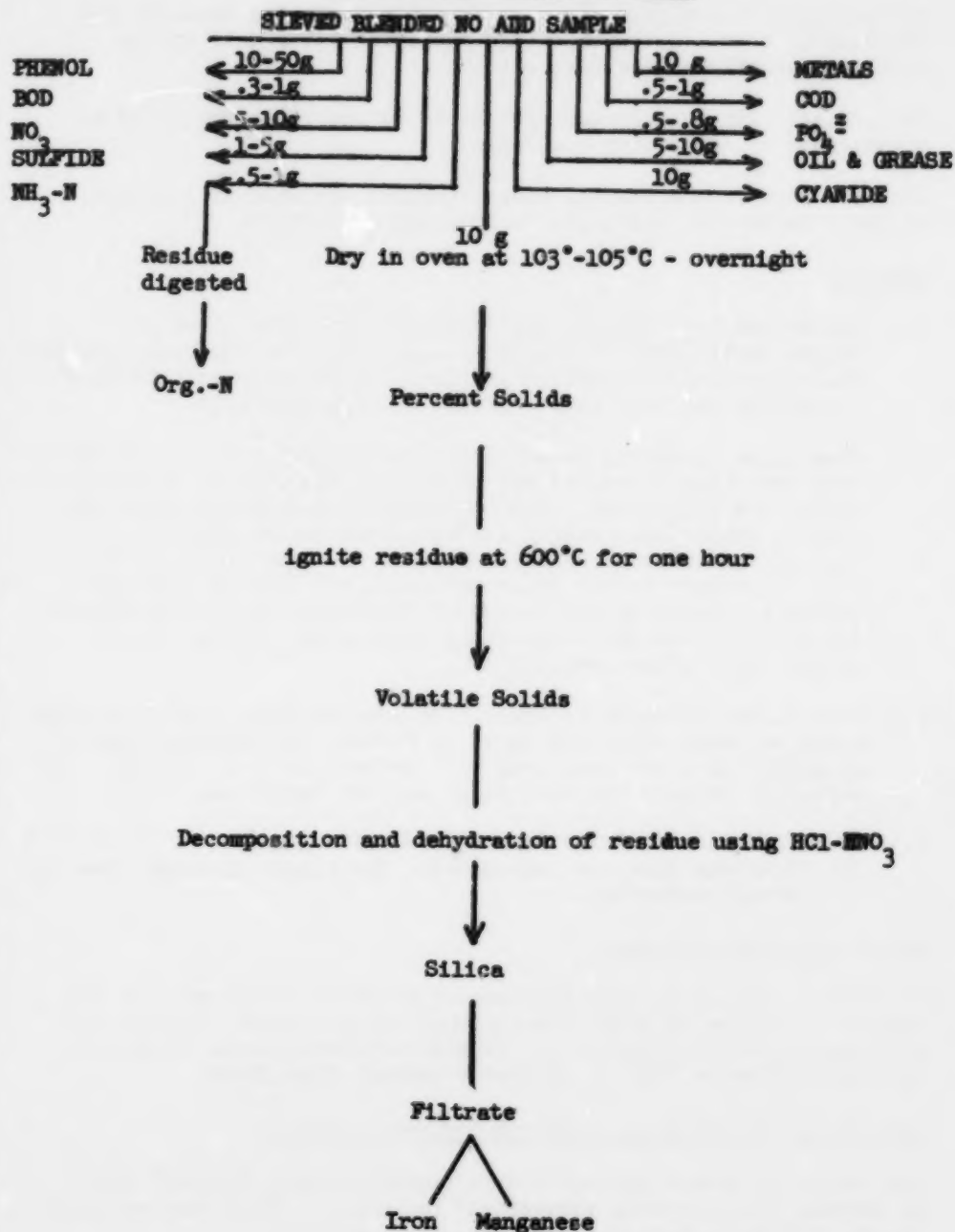


FIGURE 1

Introduction to Bottom Sediment Analysis

5. Schematic Analysis

If the sample has been frozen, thaw the sample and proceed with preparation of sample. Several portions of the wet, sieved, blended sample are weighed depending on the parameter concentration expected (Figure 1). The amount of sample necessary for any given test is determined by the analyst based on test sensitivity and concentration in the sample examined.

- 5.1 One weighed portion of wet sample is placed on aluminum strips for the BOD test.
- 5.2 A portion of the sample is weighed for the COD test. Fifty ml of distilled water is added, followed by three drops of concentrated sulfuric acid. The acid preserves the sample until the analysis can be completed.
- 5.3 A portion of the wet sample is weighed for nitrate determination. Approximately 50 ml of distilled water are added and the sample preserved with sulfuric acid for later analysis. The procedure used for nitrates is the Modified Brucine Method as in Standard Methods, 12th Ed., pp 393-394 or the automated method using a reduction column, sulfanilic acid and naphthylamine hydrochloride.
- 5.4 A portion of the wet sample is weighed for $\text{NH}_3\text{-N}$ and Org-N and approximately 50 ml of water are added with three or four drops of concentrated sulfuric acid for preservation and ammonia stabilization. The sample is analyzed using the distillation method for ammonia nitrogen followed by a Kjeldahl digestion on the residue with subsequent neutralization and distillation. An aliquot of the distillate is nesslerized and read on a spectrophotometer and reported as Org-N. NOTE: Samples are distilled into 0.02 N H_2SO_4 .
- 5.5 A portion of the wet sample is weighed and percent total solids, volatile solids, silica, manganese, and iron are determined. Total solids are determined by drying the sample overnight at $103^\circ\text{-}105^\circ\text{C}$. The fixed solids are determined by ignition in a muffle furnace at 600°C for an hour. Volatile solids are determined by calculation. A silica analysis is then made on the residue (Fixed Solids). An aliquot of filtrate from the silica determination is analyzed for iron using the Phenanthroline Method described in Standard Methods, 12th Edition, pp 156-159. Another aliquot of the filtrate is analyzed for manganese using the Persulfate Method described in Standard Methods, 12th Edition pp 489-492 with modifications as shown in procedures.

Introduction to Bottom Sediment Analysis

- 5.6 A portion of the wet sample is weighed for determination of phosphorus (as P_4). Due to the incomplete oxidation of the large amounts of organic matter present by the persulfate-sulfuric acid mixture, a dry ash method using $Mg(NO_3)_2 \cdot 6H_2O$ was found to accomplish complete oxidation. After ashing, the Potassium Antimonyl Tartrate Method is used and the resulting color development read on a spectrophotometer.
- 5.7 A portion of the wet sample is weighed for oil and grease analysis. A procedure, which is essentially the same as in Standard Methods, 12th Edition, pp. 531-532, is employed.
- 5.8 For special studies, a portion of the wet sample is weighed for long-term BOD determination in the same manner as the 5-day BOD analysis. The long-term BOD's are checked for DO content at various intervals over a period of 30 days. A DO analyzer is used to measure this parameter. One-inch glass rods are added to the DO bottle after each electrode insertion to return liquid level to a point where a water seal can be maintained upon cap replacement. By the use of a DO analyzer, a long-term BOD analysis can be made using a single bottle throughout the entire period of 30 days.
- 5.9 A portion of the wet sample is weighed for determination of cyanide. The procedure used for cyanide is Colorimetric Method as in Standard Methods, 12th Ed., pp 455-457, with minor modifications as described in procedure.
- 5.10 A portion of the wet sample is weighed for determination of phenol. The method used for phenol is essentially the same as in Standard Methods, 12th Ed., pp 517-519.
- 5.11 A portion of the wet sample is weighed for determination of metals. The procedures used for metals are new or modified methods developed by the Lake Michigan Basin Office - FWPCA.
- 5.12 A portion of the wet sample is weighed for determination of sulfide. The procedure used for sulfide is a modified method developed by the Lake Michigan Basin Office - FWPCA.
- 5.13 A portion of the wet sample is weighed for determination of chlorine demand. The method used for chlorine demand is essentially the same as in Standard Methods, 12th Ed., pp 112-114.

6. References

Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965.

CHEMICAL OXYGEN DEMAND OF BOTTOM SEDIMENTS

1. General Discussion

(See Standard Methods, 12th Ed., p. 510-11, 1965)

2. Apparatus

Reflux apparatus, consisting of 250 ml Erlenmeyer flasks with ground-glass 24/40 neck* and 300 mm jacket Liebig, West, or equivalent condensers** with 24/40 ground-glass joint, and a hot plate with sufficient power to produce at least 9 watts/sq. in. of heating surface, or equivalent, to insure an adequate boiling of the contents of the refluxing mixture.

3. Reagents

- 3.1 Sulfuric acid reagent, conc. H_2SO_4 .
- 3.2 Silver sulfate is dissolved in the H_2SO_4 acid.
- 3.3 Mercuric sulfate, analytical grade crystals
- 3.4 Ferroin indicator solution, 0.025 M: Dissolve 1.485 g 1,10-phenanthroline monohydrate, together with 0.695 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water and dilute to 100 ml. This indicator solution may be purchased already prepared.
- 3.5 Standard potassium dichromate solution, 0.500N: Dissolve 12.259 g $\text{K}_2\text{Cr}_2\text{O}_7$, primary standard grade, previously dried at 103°C for 2 hours, in distilled water and dilute to 1000 ml.
- 3.6 Standard ferrous ammonium sulfate, 0.500N: Dissolve 98 g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in distilled water. Add 20 ml conc. H_2SO_4 , cool and dilute to 1000 ml. This reagent must be standardized daily.
- 3.7 Standardization of ferrous ammonium sulfate: Dilute 25 ml standard potassium dichromate solution to approximately 250 ml. Add 50 ml conc. H_2SO_4 and allow to cool. Titrate with the ferrous ammonium sulfate titrant, using 2 or 3 drops of ferroin indicator.

$$\text{Normality} = \frac{\text{ml } \text{K}_2\text{Cr}_2\text{O}_7 \times .25}{\text{ml } \text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2}$$

* Corning 5000 or equal

** Corning 2360, 91548, or equal

4. Procedure

- 4.1 Add 25 ml $K_2Cr_2O_7$ (0.250N) to a suitable sized sample (0.5g-1.0g) of bottom sediment that will consume one-half of the $K_2Cr_2O_7$.
- 4.2 Add 1.0 g $HgSO_4$ and 0.75 g Ag_2SO_4 .
- 4.3 Add 50 ml of distilled water.
- 4.4 Add 75 ml conc. H_2SO_4 (cautiously) and mix thoroughly.
- 4.5 Add boiling stones and reflux for 2 hours.
- 4.6 Cool and rinse condenser with distilled H_2O (approximately 50 ml) while condenser is still connected to flask.
- 4.7 Disconnect and add approximately 150 ml distilled H_2O . Cool to room temperature and then titrate (after adding 3 to 5 drops ferrion indicator) to end point (the color changes sharply from blue-green to reddish-brown).
- 4.8 For standard, use 25 ml $K_2Cr_2O_7$ + 50 ml conc. H_2SO_4 and dilute to approximately 250-300 ml. Cool and titrate.

For blank, use 25 ml $K_2Cr_2O_7$, 75 ml H_2SO_4 , 50 ml distilled H_2O , 1 g $HgSO_4$, 0.75 g Ag_2SO_4 ; reflux for 2 hours and continue in the same manner as the sample.

5. Calculations

5.1 Wet basis

$$mg/kg = \frac{(a-b)c \times 8}{\text{grams sample}} \times 1000$$

5.2 Dry basis

$$mg/kg = \frac{mg/kg \text{ wet basis}}{\% \text{ solids}}$$

* a = mls of $Fe(NH_4)_2(SO_4)_2$ required for blank

b = " " " " sample

c = normality of $Fe(NH_4)_2(SO_4)_2$

6. Reference

Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965, 510-511.

CYANIDE IN BOTTOM SEDIMENTS

1. Scope

Principle: Simple cyanide salts will form hydrogen cyanide under acidic conditions. Hydrogen cyanide has a boiling point of 26°C and can be easily isolated by distillation. On the other hand, some complex cyanides are not easily decomposed and others, such as cobaltcyanides are essentially non-responsive to this test. However, the conversion can be hastened by the addition of magnesium and mercuric salts.

2. Summary of Method

The liberated cyanides are converted to sodium salts and reacted with chloramine T under slightly alkaline conditions to form cyanogen chloride. A pyridine-pyrazolone reagent reacts with the cyanogen chloride to form a blue dye, the absorbance of which is measured at 620 mμ. Increased sensitivity can be obtained by extracting the dye into n-butyl alcohol and reading the absorbance at 630 mμ.

3. Interference

Most of the substances known or thought to interfere can be removed via the distillation procedure. Common interferences are heavy metal ions, thiocyanates, cyanate, and other substances which may form cyanide. Sulfides and fatty acids interfere with the analysis and are not eliminated by distillation. However, these materials are not often found in surface waters. If they are known to be present, procedures for their removal are listed in the 12th Edition Standard Methods, 1965.

4. Minimum Detectable Concentration

The minimum detectable concentration is 0.02 mg/l as cited in the 12th Edition Standard Methods, 1965.

5. Apparatus

- 5.1 Modified Claissen flask, 1,000 ml.
- 5.2 Allihn condenser. (200 mm)
- 5.3 Gas washer bottles (Sargent #39623) or equivalent.
- 5.4 Suction flask, 500 ml.
- 5.5 Water aspirator, air inlet tube.
- 5.6 Heating element, for modified Claissen flask or bunsen burner.

Cyanide in Bottom Sediments

- 5.7 pH meter.
- 5.8 Reaction tubes (test tubes).
- 5.9 Spectrophotometer or filter photometer providing a 1 cm light path (or longer) and a wave length of 630 mμ.

6. Reagents

- 6.1 Sulfuric acid, conc.
- 6.2 Sodium hydroxide, IN: Dissolve 4 g NaOH in 100 ml of water.
- 6.3 Mercuric chloride solution: Dissolve 34 g of HgCl_2 in 500 ml of distilled water.
- 6.4 Magnesium chloride solution: Dissolve 51 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in 100 ml of distilled water.
- 6.5 Acetic acid, glacial.
- 6.6 Chloramine T, 1.0% aqueous solution. (Prepare daily. If reagent does not dissolve readily, degradation of the reagent is indicated and it should be replaced.)
- 6.7 1-phenyl-3-methyl-5-pyrazolone, saturated aqueous solution (7 g/l) (Eastman Reagent #1397).
- 6.8 Bis-pyrazolone: Dissolve 0.025 g in 25 ml pyridine. Prepare fresh daily. (Eastman reagent #6969).
- 6.9 Mixed reagent immediately prior to use; mix 125 ml of reagent #6.7 with 25 ml of reagent #6.8.
- 6.10 Stock cyanide standard: Dissolve 0.251 g KCN in one liter of distilled water (add two pellets of sodium hydroxide for stability). Solution contains 0.1 mg/ml cyanide. This is a primary standard and must be prepared fresh each week.
- 6.11 Working Standard: Dilute stock standard 100 fold, 1 ml = 1 μg. Take 0 - 5 ml of the resulting solution for standard curve. Prepare fresh daily.

Cyanide in Bottom Sediments

6.12 5% disodium hydrogen phosphate.

6.13 N-butyl alcohol - reagent grade.

6.14 The buffer solution is prepared by adding 35.0 ml 0.1 N. NaOH to 50.0 ml 0.1M KH_2PO_4 and diluting to 100 ml. This buffer gives a pH of 7.2.

The water used in preparing both solutions should be free of carbon dioxide. This can be accomplished fairly well by heating distilled water to boiling in a flask and cool while stoppered lightly. If stopper is tight while water is hot, cooling may freeze the stopper.

7. Procedure

7.1 Distillation: An aliquot of a well-mixed bottom sediment sample, containing not more than 500 mg of cyanide (10g) is added to a Claissen flask and brought to approximately 500 ml with distilled water. Fifty ml of 1.0 N sodium hydroxide and 75 ml of distilled water are added to the gas washer receiving vessel and the unit is assembled. Air, drawn through the unit via vacuum aspiration, is adjusted so that its flow rate is approximately one bubble per second through the receiving unit, or as many as necessary to prevent flow back.

After the air inlet tube is positioned, 1.0 ml of mercuric chloride and 4.0 ml of magnesium chloride solutions are added through the tube and two minutes are allowed for mixing. After rinsing the tube with distilled water, 5 ml of concentrated sulfuric acid are then added through the tube; at this point, if it is not known whether the pH is 2.0 or lower, the pH should be determined on a separate volume of the sample with the same amount of sulfuric acid added as in the distilled sample.

Heat is applied to the system at a rate that will produce boiling, as soon as possible but will not allow a flow back. Refluxing, which should begin within 30 minutes, is carried on for 1½ hours. Occasionally during distillation the air flow rate may have to be readjusted to prevent the reverse flowing of the sample solution.

Cyanide in Bottom Sediments

7. Procedure (continued)

7.1 (continued)

When the heating is discontinued, the air flow proceeds for an additional 15 minutes for cooling purposes.

- 7.2 The contents of the gas washer vessel are drained into a 250 ml volumetric flask and the accessible components of the distillation unit rinsed twice with distilled water. The washings are added to the distillate and the solution brought to volume.

Pipette a 15 ml aliquot-or other suitable volume- of the solution into a 25 ml volumetric flask.

Neutralize to phenolphthalein end-point using acetic acid (1:4 or weaker).

Add 0.2 ml Chloramine-T, stopper, mix, and after one minute, add 2 ml of the buffer solution.

Add 5 ml of the mixed pyrazolone, dilute the solution to volume with distilled water, stopper, mix, and allow to stand for 20 minutes for color development.

The optical densities of the standard and samples are read against a reagent blank at 620 mμ on a spectrophotometer within one hour, at maximum.

- 7.3 Alcohol extraction: The sensitivity of detection is slightly increased by determining the optical density of the colored dye in butyl alcohol. Some interferences which may pass through the distillation may also be eliminated.

After color development in the aqueous system, add 2 ml of disodium hydrogen phosphate solution and 10 ml of n-butyl alcohol. Mix and withdraw an aliquot of the alcohol layer. Measure optical density at 630 mμ.

- 7.4 Samples are to be compared with distilled standards.

8. Calculation

8.1 Wet Basis:

$$\text{mg/kg CN}^- = \frac{\text{mg in Std.}}{\text{O.D. Std.}} \times \frac{\text{O.D. Sample}}{(\text{grams sample in aliquot})} \times 1,000$$

8.2 Dry Basis

$$\text{mg/kg CN}^- = \frac{\text{mg/kg wet basis}}{\% \text{ Solids (decimal fraction)}}$$

9. References

- 9.1 Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965, 448-457.
- 9.2 Ludzack, et al., Analytical Chemistry 26: 1784 (1954).
- 9.3 Jarrell, R., Report, Colorado River Basin Project Laboratory.
- 9.4 Recovery of Cyanide by a Modified Surface Distillation, Charles T. Elly, Unpublished.
- 9.5 Babcock, R., American Oil Co., Unpublished Report.

TOTAL AND SOLUBLE FERROUS IRON IN BOTTOM SEDIMENTS**1. General Discussion**

- 1.1 Principle: Iron is brought into solution and reduced to the ferrous state by boiling with acid and hydroxylamine, and treated with 1,10-phenanthroline at pH 3.2-3.3. Three molecules of phenanthroline are required to chelate each atom of ferrous iron to form an orange-red complex. The colored solution obeys Beer's law; its intensity is dependent upon pH and is stable for at least 6 months. A pH between 2.9 and 3.4 insures rapid and maximum color development in the presence of an excess of phenanthroline.
- 1.2 Interference: Among the interfering substances are strong oxidizing reagents, cyanide, nitrite, and phosphates - polyphosphates more so than orthophosphate; chromium; zinc in concentrations exceeding ten times that of iron; cobalt and copper in excess of 5 mg/l, and nickel in excess of 2 mg/l. Bismuth, cadmium, mercury, molybdate, and silver precipitate phenanthroline. The initial boiling with acid reverts polyphosphates to orthophosphate and removes cyanide and nitrite, which would otherwise interfere. The addition of more hydroxylamine will eliminate errors caused by excessive concentrations of strong oxidizing reagents. In the presence of interfering metal ions, a larger excess of phenanthroline is required to replace that which is complexed by these interferences. With excessive concentrations of interfering metal ions, the extraction method is preferred.

If much color or organic matter is present, it may be necessary to evaporate the sample, gently ash the residue, and then redissolve in acid. The ashing may be carried out in silica, porcelain, or platinum crucibles which have previously been boiled for several hours in 1 + 1 HCl.

- 1.3 A separate sediment sample must be taken for ferrous iron, preserved with 12 ml conc. HCl per 300 ml bottle, if sample is not preserved by freezing.

2. Apparatus

- 2.1 Colorimetric equipment: One of the following is required:
- a. Spectrophotometer, for use at 510 mμ, providing a light path of 1 inch or longer.
 - b. Filter photometer, providing a light path of 1 inch or longer and equipped with a green filter having maximum transmittance near 510 mμ.
- 2.2 Hot Plate.
- 2.3 Centrifuge and 50 ml tubes with caps.
- 2.4 Magnetic Stirrer.

Total and Soluble Ferrous Iron in Bottom Sediments

- 2.5 Acid-washed glassware: All glassware must be washed with conc. HCl and rinsed with distilled water prior to use, in order to remove the thin film of adsorbed iron oxide which is frequently present as a result of employing the glassware for other purposes.

3. Reagents

All reagents must be low in iron. Iron-free distilled water is required. Glass-stoppered bottles are recommended for storage. The hydrochloric acid, ammonium acetate solution, and stock iron solutions are stable indefinitely, if tightly stoppered. The hydroxylamine and phenanthroline solutions are stable for several months. The standard iron solutions are not stable and must be prepared fresh, as needed, by diluting the stock solution. Visual standards in nessler tubes are stable for 3 months if protected from light.

- 3.1 85% Phosphoric Acid.
- 3.2 Hydrochloric Acid, conc.
- 3.3 Hydrochloric Acid, 1 / 1 (oxygen free H₂O).
- 3.4 Hydroxylamine solution: Dissolve 10 g NH₂OH.HCl in 100 ml distilled water.
- 3.5 Ammonium acetate buffer solution: Dissolve 250 g NH₄C₂H₃O₂ in 150 ml distilled water. Add 700 ml glacial acetic acid and dilute to 1 liter. (Since even good grade NH₄C₂H₃O₂ contains a significant amount of iron, new reference standards should be prepared with each buffer preparation.)
- 3.6 Phenanthroline solution: Dissolve 0.1 g 1,10 phenanthroline monohydrate, C₁₂H₈N₂·H₂O in 100 ml distilled water by stirring and heating to 80°C; do not boil. Discard the solution if it darkens. Heating is not necessary if 2 drops of conc. HCl are added to the distilled water. (Note that 1 ml of this reagent is sufficient for no more than 0.1 mg Fe.)
- 3.7 Stock iron solution: The metal (a) or the salt (b) may be used for the preparation of the stock solution, which contains 0.200 mg Fe per 1.00 ml.
- a. Use electrolytic iron wire, or "iron wire for standardizing," to prepare the solution. If necessary, clean the wire with fine sandpaper to remove any oxide coating and to produce a bright surface. Weigh 0.2000 g wire and place in a 1-liter volumetric flask. Dissolve in 20 ml 6N H₂SO₄ and dilute to the mark with iron-free distilled water.

Total and Soluble Ferrous Iron in Bottom Sediments

- b. If ferrous ammonium sulfate is preferred, add slowly 20 ml conc. H_2SO_4 to 50 ml distilled water and dissolve 1.404 g $Fe(NH_4)_2(SCO_4)_2 \cdot 6H_2O$. Add dropwise 0.1N $KMnO_4$ until a faint pink color persists. Dilute with iron-free distilled water to 1,000 ml and mix.
 - 3.8 Standard iron solutions: These should be prepared the day they are used.
 - a. Pipet 50.00 ml stock solution into a 1-liter volumetric flask and dilute to the mark with iron-free distilled water; 1.00 ml = 10.0 μg Fe.
 - b. Pipet 5.00 ml stock solution into a 1-liter volumetric flask and dilute to the mark with iron-free distilled water; 1.00 ml = 1.00 μg Fe.
 - 3.9 Ammonium hydroxide (1:1).
 - 3.10 Standard potassium dichromate solution, 0.25 normal (use oxygen-free H_2O).
 - 3.11 Diphenylamine sulfonate indicator solution. Prepare by dissolving 3.17g of barium diphenylamine sulfonate in distilled water and adding a solution of 1.7g of sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$) to precipitate the barium and dilute to one liter with oxygen-free H_2O .
 - 3.12 Oxygen-free water.
 - 3.13 Ferrous ammonium sulfate approximately 0.25N (use oxygen-free H_2O).
4. Procedure - Total Iron
 - 4.1 Weigh 10 grams of a well-mixed sediment sample into 400 ml beaker and add 5 ml HNO_3 , 0.5 ml H_2O_2 (30%), plus 1 ml $NaNO_3$ (4%), and evaporated to dryness.
 - 4.2 Ash in muffle furnace at 550°C for 50 minutes.
 - 4.3 Cool, add 40 ml HCl (1:1), cover with watch glass, and heat gently for 20 minutes.
 - 4.4 Allow to stand 5 minutes to cool (or longer) and filter into a 100 ml volumetric flask.
 - 4.5 Dilute to volume, mix, and take 50 ml or an aliquot containing 0.25 mg iron (diluted to 50 ml) into a 100 ml volumetric flask.
 - 4.6 The sample is then made alkaline to phenolphthalein (1 drop) with ammonium hydroxide (1:1).

Total and Soluble Ferrous Iron in Bottom Sediments

- 4.7 Add 2 ml HCl, 2 ml hydroxylamine hydrochloride solution and boil, reducing the volume to approximately 20 ml.
- 4.8 Add 10 ml acetate buffer*, 10 ml phenanthroline solution and dilute to 100 ml. Mix thoroughly and allow 15 minutes for maximum color development. Read adsorbance against a blank at a wave length of 510 mμ on a spectrophotometer.
- 4.9 Calculations are as shown in "6" below.
5. Procedure - Soluble Ferrous Iron
 - 5.1 Weigh 10 grams of a well-mixed sediment sample into a 250 ml beaker, add 100 ml of oxygen-free distilled water and digest on hot plate for 30 minutes.
 - 5.2 Filter into a 100 ml volumetric flask.
 - 5.3 Dilute to volume, mix and take 50 ml or an aliquot containing 0.25 mg of iron (diluted to 50 ml) into a 100 ml volumetric flask.
 - 5.4 Then proceed as in total iron sections 4.6 and 4.8
6. Calculation
 - 6.1 Wet basis

$$\text{mg/kg} = \frac{\text{mg Std.}}{\text{O.D. Std.}} \times \frac{\text{O.D. Sample}}{\left(\frac{\text{grams sample}}{\text{in aliquot}} \right)} \times 1000$$
 - 6.2 Dry basis

$$\text{mg/g} = \frac{\text{mg/g wet basis}}{\% \text{ solids (decimal fraction)}}$$

* Check pH of solution sample on pH meter. Range should be 2.9-3.4 units for good color development.

Total and Soluble Ferrous Iron in Bottom Sediments

7. Procedure - Total Ferrous Iron by Titration

- 7.1 Weigh an 8-10 gram sample of well-mixed sediment in a 150 ml beaker and add sufficient hydrochloric acid to extract the expected iron concentration, 10 ml of 85 percent phosphoric acid, plus enough oxygen-free water to bring total volume to approximately 50 ml.
- (a) For each mg of total iron expected add 1.2 mg of HCl plus a 10 percent excess. (20 ml 1 $\frac{1}{2}$ 1 HCl)
 - (b) In moderately dilute solution and at room temperature, dichromate does not react with chloride ion.
 - (c) Phosphoric acid is added for two reasons:
 - (1) To complex any ferric ion initially present in the specimen, thus preventing its reduction to the ferrous state by hydrogen sulfide during extraction.
 - (2) To prevent the indicator from changing color before reaching equivalence point by increasing oxidation potential to $- .85$.
- 7.2 Boil on a hot plate for 15 minutes. Take care to avoid frothing by adding more deoxygenated water or by removing from heat and stirring.
- Note: Volume must be 50 mls or less at conclusion of 15-minute boiling period.
- 7.3 Transfer and rinse with small aliquots of deoxygenated water into a 50 ml centrifuge tube with cap and centrifuge for 10 minutes.
- 7.4 Decant solution into a 500 ml Erlenmeyer flask containing approximately 200 ml of oxygen-free water. Rinse centrifuge tube with small aliquots of water.
- 7.5 Add 1 ml of indicator solution. Titrate with standard dichromate until the first permanent coloration appears.

Total and Soluble Ferrous Iron in Bottom Sediments

8. Calculation

$$\text{Iron, mg/kg} = \frac{(A - B) C \times 55.9}{D} \times 1000$$

A = milliliters $K_2Cr_2O_7$ solution required to titrate sample

B = milliliters $K_2Cr_2O_7$ to titrate blank

C = normality of $K_2Cr_2O_7$

D = grams sample used (dry basis)

9. References

- 9.1 Patterson, A., Thomas, H.C., Quantitative Analysis, Henry Holt and Co., New York 1952, pp 278-287.
- 9.2 Fisher, R.B., Quantitative Chemical Analysis, W.B. Saunders Co., Philadelphia, 1957, pp 284-5.
- 9.3 Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965, 156-159.

METALS IN BOTTOM SEDIMENTS

Atomic Absorption

1. General Discussion

Metal complexes are freed by digestion of bottom sediment samples with concentrated HNO_3 acid H_2O_2 (30%). A wide range of elements can be determined by atomic absorption with the selection of the proper source (hollow cathode lamp).

1.1 Principle: The principle of atomic absorption and its application to the analysis of metals is based upon the element of interest being dissociated from its chemical bonds and placed into an unexcited, un-ionized "ground" state. It is then capable of absorbing at discrete lines of narrow band width radiation provided by a hollow cathode lamp with a cathode made of the element being sought. The absorption of the light by the metal in the ground state is related to the concentration of the metal being sought.

1.2 Interference: The atomic absorption method is relatively free of interferences.

2. Apparatus

2.1 Atomic absorption spectrophotometer.

2.2 Muffle furnace.

2.3 Pipettes.

2.4 250 ml beakers.

2.5 Watch glasses.

2.6 250 ml volumetric flasks.

2.7 Polyethylene bottles (60 ml).

2.8 Centrifuge (20,000 rpm).

3. Reagents

3.1 Nitric acid (conc. metal-free).

3.2 Hydrogen peroxide (30%).

3.3 Hydrochloric acid (conc. metal-free).

Metals in Bottom Sediments- Atomic Absorption

- 3.4 Ammonium chloride.
- 3.5 Calcium nitrate.
- 3.6 Redistilled water or double deionized water (metal-free).
- 3.7 Bottled acetylene gas.
- 3.8 Bottled nitrous oxide gas.
- 3.9 Compressed air.

4. Preparation of Standards

- 4.1 Using a commercial certified atomic absorption standard, containing 1,000 mg/l of the metal, prepare an appropriate dilute stock standard. Standards may be prepared in the laboratory using pure metals.
- 4.2 Make up working standards to approximate the concentration in the sample using the dilute stock standard.

5. Preparation of Samples

- 5.1 Place 2.5 g of a well mixed bottom sediment sample in a 250 ml beaker, add 10 ml of conc. HNO_3 acid and 0.5 ml of H_2O_2 (30%) and evaporate to dryness.
- 5.2 Ash at $400-425^\circ\text{C}$ for one hour in a muffle furnace and cool.
- 5.3 Add 25 ml of acid mixture (200 ml of conc. HNO_3 , 50 ml conc. HCl and 750 ml of redistilled water), 20 ml of 10% NH_4Cl and 1 ml of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (11.8 g/100 ml). Heat gently for 15 minutes and cool for five minutes or longer.
- 5.4 Transfer sample to centrifuge tube and centrifuge for 10 minutes at 20,000 rpm. Transfer the supernatant to a 250 ml volumetric flask. Rinse the residue in the centrifuge tube twice with redistilled water and add washings to supernatant and dilute to volume. Then transfer sample to a small plastic bottle.

6. Method for Cu, Cd, Ni, Zn, Cr, Pb, Mn, Al and Other Metals

Follow procedures as outlined in manufacturer's manual.

Metals in Bottom Sediments -Atomic Absorption

7. Calculations

7.1 Wet Basis

By use of table from manufacturer's manual, convert percent absorption to absorbance.

$$\text{mg/kg} = \frac{\text{mg/l in std.}}{\text{absorbance of std.}} \times \text{dil. factor} \times \text{absorbance of sample} \times \frac{1,000}{\text{g of sample/L}}$$

7.2 Dry Basis

$$\text{mg/kg} = \frac{\text{mg/kg wet basis}}{\% \text{ solids (decimal fraction)}}$$

8. Atomic absorption is the preferred method because it is much faster, more accurate and there are less interferences.

METALS IN BOTTOM SEDIMENTS

Polarographically

1. General Discussion

Metal complexes are freed by digestion of / ^{sediment} with HNO_3 acid. Simultaneous determination of copper, cadmium, nickel, and zinc is possible, also a wide range of other elements can be determined polarographically with the selection of the proper supporting electrolyte.

1.1 Principle: Cations are reduced on the surface of a dropping mercury electrode to form an amalgam in a current producing reaction. This current is reflected in a galvanometer and may be recorded as a measurable wave which is **proportional to** the concentration of a specific cation that is being reduced at its specific half-wave potential. The wave height produced by an unknown is compared to that made by a known standard for determining the amount of an unknown metal in the sample.

1.2 Interference: Any volatile or organic interference is eliminated by the ashing process in which carbon is destroyed. In addition, iron, chromium, turbidity, chlorides, oxidizing, and reducing substances, and dissolved oxygen are major interferences that are likely to be encountered. The following procedures are designed to eliminate or reduce to a minimum these types of interferences.

1.3 Precautions: The one most precautionary measure to take is the washing of all glassware and other containers with hot HCl (1:1) and rinse with distilled water. Etched beakers should be avoided since they could possibly retain metals. Any wasted mercury should be removed to prevent the poisonous fumes from volatilizing into the air.

2. Apparatus

- 2.1 Sargent Model XV Recording Polarograph
- 2.2 MicroRange Extender
- 2.3 Muffle Furnace
- 2.4 Pipettes (Mohr and Volumetric)
- 2.5 600 ml Beakers
- 2.6 Watch Glasses (to cover 600 ml beakers)
- 2.7 10 ml Beakers
- 2.8 Hot Plate
- 2.9 50 ml Volumetric Flask
- 2.10 Folded Filter Paper (Whatman #12, 18.5 cm or equivalent)
- 2.11 Polyethylene Bottles (60 ml, 2 liter, and wash bottles)

3. Reagents (Not mentioned in procedures)

- 3.1 Mercury (high-grade, metal-free)
- 3.2 Nitric Acid (conc., metal-free)
- 3.3 Hydrochloric Acid (conc., metal-free)
- 3.4 Redistilled Water (metal-free, stored in polyethylene bottles)
- 3.5 Sodium Sulfite, reagent grade
- 3.6 Bottled Nitrogen Gas (water-pumped)

4. Preparation of Standards

- 4.1 A stock standard solution is made by dissolving the salts of the metals in water or the metals in nitric acid in such proportions that 1.0 ml of standard equals 0.010 mg of each of the six metals (Cu, Cd, Ni, Zn, Pb, and Cr).
- 4.2 A working standard is prepared by diluting 100 ml of stock standard to 1 liter. 5.0 ml contains 0.005 mg of each of the metals.
- 4.3 A 5.0 ml portion of the working standard is pipetted into a 10 ml beaker and evaporated to dryness. This standard is treated exactly as the samples and the comparative wave heights are used in calculating the amount of the particular metal in the samples.

5. Preparation of Bottom / Sediment Samples for Metals on the Polarograph

- 5.1 To a 10 gram sample of well-mixed bottom mud in a 600 ml beaker, add 10 ml HNO_3 (conc.) and 0.5 ml H_2O_2 (30%) and evaporate to dryness. (If sample is not very uniform, use 20 grams.)
- 5.2 Ash at 450-500° for 30 minutes in muffle furnace and cool.
- 5.3 Add 25 ml acid mixture, 200/ HNO_3 conc. + 50 ml HCl conc. + 750 ml redistilled water, heat gently 15 minutes and cool 5 minutes or longer.
- 5.4 Filter and dilute the filtrate to 50 ml in volumetric flask, then transfer to a small plastic sample bottle.
- 5.5 Pipette three 5 ml portions into 10 ml beakers and evaporate to dryness for analysis.

6. Method for Cu, Cd, Ni, and Zn on the Polarograph

- 6.1 Reagents: Prepare all reagents in metal-free distilled water.
 - a. Electrolyte: Dissolve 107 grams of NH_4Cl , 11.4 grams $(\text{NH}_4)_2\text{CO}_3$, and 67 ml $\text{NH}_4(\text{OH})_2$ in distilled water. Add 10 ml of 0.2% triton-X and dilute to 1 liter. The strength of this solution is 2.0M NH_4Cl , 0.1M $(\text{NH}_4)_2\text{CO}_3$, and 1M NH_4OH .

- b. Sulfuric Acid (1:5).
- c. Sodium Sulfite Solution (saturated)
- d. Water-pumped Nitrogen Gas (This gas passed through a saturated solution of sodium sulfite just prior to use.)

6.2 Procedure

- a. To the dried sample or standard, add 2 drops H_2SO_4 (1:5) and heat gently until near dryness.
- b. Heat strongly until fumes cease.
- c. Cool, add 5.0 ml electrolyte and allow 5 minutes contact time.
- d. Police the beaker and transfer sample to cell.
- e. Add 5 drops sodium sulfite solution and allow nitrogen gas* to flow through cell for one minute.
- f. Add Mercury pool and, if any air bubbles are present, swirl gently to remove.
- g. Record polarogram.
- h. Recommended settings: Sensitivity 0.002 (if range extender is available, otherwise use 0.003), voltage range 0 to -2. Compensation and damping should not be used unless necessary.

7. Method for Lead on the Polarograph

The normal interference of iron is minimized by the use of hydroxylamine hydrochloride in this method.

7.1 Reagents

- a. ~~Electrolyte~~ - 0.1M KCl
- b. Hydroxylamine-hydrochloride - 10%
- c. Hydrochloric acid - 1:25
- d. Water-pumped nitrogen gas (passed through saturated sodium sulfite just prior to use)

* The nitrogen gas is first washed by passing through a flask containing sodium sulfite (saturated).

7.2 Procedure

- a. To the dried sample or standard, add 1.0 ml KCl (1:25) and heat gently for about 3 minutes (heat must be such that solution does not go to dryness).
- b. Add 2 drops hydroxylamine-hydrochloride solution and heat 3 more minutes (again solution must not go to dryness). If a yellowish color due to high iron content persists, add hydroxylamine hydrochloride dropwise until the color disappears and heat for 1 more minute.
- c. Remove, cool, and add 5.0 ml electrolyte.
- d. Police, transfer to cell, and allow nitrogen gas to flow through sample for 5 minutes.
- e. Add mercury pool and record polarogram, using nitrogen blanket.
- f. Recommended settings: Sensitivity -0.001, compensation and damping as needed.

8. Method for Total Chromium (10)

This method is based upon the oxidation of chromium by alkalibromite and the simultaneous precipitation of the normally interfering iron.

8.1 Reagents:

- a. Oxidizing solution - 100 ml 0.5N NaOH solution mixed with 5 ml saturated bromine water.
- b. Electrolyte - 0.2N NaOH solution and 0.1 g gelatin/liter.
- c. Sodium sulfite - saturated anhydrous solution.
- d. Nitrogen gas - water pumped.

8.2 Procedure

- a. To the dried sample or standard, add 0.4 ml oxidizing solution and heat for 2 minutes on hot plate just below boiling.
- b. Remove and allow to cool for 5 minutes or longer.
- c. Add 5.0 ml electrolyte and transfer to cell, policing.
- d. Add 2 drops sodium sulfite solution and allow nitrogen gas to flow through sample for 5 minutes.
- e. Add mercury pool and record polarogram, using nitrogen blanket.
- f. Recommended settings: Sensitivity -0.003, compensation -0, damping -0.

9. Calculation of Metals in / ^{bottom sediments} (or any solid material) in mg/kg

9.1 Wet Basis:

$$\text{mg/kg} = \frac{S. \text{ sample}}{S. \text{ standard}} \times \frac{H. \text{ sample}}{H. \text{ standard}} \times \frac{0.005}{1} \times \frac{1}{(\text{grams sample in aliquot})} \times 1000$$

where S = sensitivity

H = wave height in mm

0.005 = mg metal in 5 ml std. (assuming 5 ml std. and sample are used; this figure is changed if different amounts of std. are used)

solids = decimal fraction of solids in wet sediment

Example

$$\begin{array}{l} \text{wet basis} \\ \text{mg/kg} \end{array} = \frac{0.006}{0.002} \times \frac{56}{25} \times \frac{0.005}{1} \times \frac{1}{(\text{grams sample in aliquot})} \times 1000$$

9.2 Dry Basis:

$$\text{mg/kg} = \frac{\text{mg/kg wet basis}}{\% \text{ solids (decimal fraction)}}$$

Metals in Bottom Sediments - Polarographically

REFERENCES

1. Report of the Advisory Committee on Revision of the Public Health Service 1946 Drinking Water Standards. (Mimeo.)
2. Doudoroff, P. and Katz, M. Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components to Fish. II. The Metals, as Salts. *Sewage and Industrial Wastes*, 25, 802 (1953).
3. Kroner, R. C., Ballinger, D. G., and Kramer, H.P. Evaluation of Laboratory Methods for Analysis of Heavy Metals in Water. *Journal of American Water Works Association*, 52, 117 (1960).
4. Love, S. K. Analytical Instruments Used in the Modern Water Plant Laboratory. *Journal of American Water Works Association*, 43, 731 (1951).
5. Wyatt, J. W. Instrumentation in the Laboratory. *Journal of American Water Works Association*, 45, 138 (1953).
6. Butts, P. G., and Mellon, M. G. Polarographic Determination of Metals in Industrial Wastes. *Sewage and Industrial Wastes*, 23, 59 (1951).
7. Lingane, J. J. Systematic Polarographic Metal Analysis Characteristics of Arsenic, Antimony, Bismuth, Tin, Lead, Cadmium, Zinc, and Copper, in Various Supporting Electrolytes. *Industrial and Engineering Chemical Analysis*. Ed. 15, 583 (1943).
8. Manzel, R. C., and Jackson, M. L. Determination of Copper and Zinc in Soils and Plants. *Analytical Chemistry*, 23, 1861 (1951).
9. Lingane, J. J., and Kolthoff, I. M. Polarographic Study of the Reaction of Chromate Ion at the Dropping Mercury Electrode. *Journal of American Chemical Society*, 62, 852 (1940).
10. Standard Method for Polarographic Determination of Lead and Chromium in Zinc. ASTM E-68-56. American Society of Testing Materials.
11. Hawkins, R. C., and Thode, H. G. Polarographic Determination of Copper, Lead, and Cadmium in High Purity Zinc Alloys. *Industrial and Engineering Chemical Analysis*, Ed. 16, 71 (1944).

Metals in Bottom Sediments - Polarographically

REFERENCES (continued)

12. McFarren, E. F., Campbell, J. E., and Engle, J. B. Variations in Zinc and Copper Content of Bivalves. (In Press).
13. Official Methods of Analysis of the Association of Official Agricultural Chemists, Ninth Edition, page 333, (1960).
14. Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965, 458-466.

1. General Discussion

- 1.1 Principle: Free ammonia nitrogen can be recovered by distillation of a sample at pH 7.4. Since natural waters exhibit varying pH values and buffering properties, a phosphate buffer is applied to maintain the required pH during the distillation process. The free ammonia distillate is collected in boric or sulfuric acid solutions to minimize ammonia losses.

Samples containing high ammonia concentrations (5-10 mg/l) should be analyzed following the procedure described in "Standard Methods for the Examination of Water and Wastewater" 12th Ed., 1965, Method A, page 191, Sec. 4.4.

The concentration of ammonia in the distillate determines the final method for measurement.

If the sample contains from 0.01 to 0.2 mg/l ammonia nitrogen, the distillate from 500 ml of sample is collected in 0.02N H_2SO_4 . The acid solution is concentrated on a steam bath to 50 ml producing a 10:1 concentration. The ammonia in the concentrated solution is then reacted with Nessler's reagent to form a characteristic yellow-brown color which is measured at a wave length of 425 m μ .

Samples which contain from 0.2 to 1.0 mg/l are distilled into dilute boric acid solution. The acid distillates are diluted to the original 500 ml volume and a 50 ml aliquot is taken for Nesslerization as outlined above.

Samples that contain more than 1.0 mg/l ammonia nitrogen are distilled into boric acid and can then be titrated with standard sulfuric acid using an appropriate indicator.

- 1.2 Interference: Ammonia recovery will be low on water samples containing more than 250 mg/l calcium unless the treatment prescribed in Sec. 4.2 is followed. The calcium and the phosphate buffer react to precipitate calcium phosphate, releasing hydrogen ions and lowering the pH. A number of aliphatic and aromatic amines, organic chloramines, acetone, aldehydes, and alcohols, and other undefined organic compounds, cause trouble in direct nesslerization. Compounds of this type have been found to yield a yellowish or greenish off color or a turbidity following the addition of nessler reagent to distillates collected from chlorinated samples.

Ammonia Nitrogen in Bottom Sediments - Distillation

The titration procedure is also subject to amine interference because the standard acid can react with such alkaline bodies. However, the titration procedure is free of interference from neutral organic compounds. Sulfide has also been reported to cause turbidity following nesslerization, a condition which may be avoided by adding lead carbonate to the flask prior to distillation. Volatile substances such as formaldehyde can be removed by boiling at low pH, after which the sample can be distilled and nesslerized in the normal manner.

2. Apparatus

- 2.1 Distillation apparatus: A glass flask of 800 ml capacity attached to a vertical condenser is so arranged that the distillate falls directly into the collecting glassware.
- 2.2 Digestion apparatus: Provided with a suction take-off to remove water vapor and sulfur trioxide fumes.
- 2.3 Colorimetric equipment: A spectrophotometer for use at 400 to 425 m μ , providing a light path of 1 inch or longer.
- 2.4 Nessler tubes: Matched 50 ml, tall forms.

3. Reagents

- 3.1 Ammonia-free water.
- 3.2 Phosphate Buffer Solution pH 7.4: Dissolve 14.3 g anhydrous potassium dihydrogen phosphate, KH_2PO_4 , and 68.8 g anhydrous dipotassium hydrogen phosphate K_2HPO_4 , and dilute to 1 liter with ammonia-free water.
- 3.3 Boric Acid Solution: Dissolve 20 g anhydrous boric acid H_3BO_3 in ammonia-free water and dilute to 1 liter.
- 3.4 Sodium Hydroxide-Sodium Thiosulfate reagent: Dissolve 500 g NaOH and 25 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in ammonia-free water and dilute to 1 liter.

- 3.5 Phenolphthalein Indicator Solution: Dissolve 5 g phenolphthalein in 500 ml 95 per cent ethyl alcohol and add 500 ml distilled water. Then add 0.02N NaOH dropwise until a faint pink color appears.
- 3.6 Mixed Indicator: Mix 2 volumes of 0.2 per cent methyl red in 95% alcohol with 1 volume of 0.2 per cent methylene blue in 95 per cent ethyl alcohol. This solution must be made fresh every 30 days.
- 3.7 Standard Sulfuric Acid Titrant 0.02N: In this strength 1.00 ml equals 0.28 mg N.
- 3.8 Nessler reagent: Dissolve 100 g mercuric iodide, HgI_2 and 70 g potassium iodide, KI, in a small quantity of ammonia-free water, and add this mixture slowly, with stirring, to a cool solution of 160 g NaOH in 500 ml ammonia-free water. Dilute to 1 liter and store in dark pyrex bottle out of sunlight. Stable about one year. (Caution Toxic)
- 3.9 Standard Ammonium Solution: Dissolve 3.819 g anhydrous ammonium chloride, NH_4Cl , dried at $100^\circ C$ in ammonia free water and dilute to 1,000 ml: 1 ml = 1.0 mg N- (1.22 mg NH_3). Then dilute 10.0 ml stock ammonium chloride solution to 1,000 ml with ammonia-free water. 1 ml = 10.00 μg N (12.2 μg NH_3).
- 3.10 Standard Organic Nitrogen Solution: Dissolve 1.0503 g of glutamic acid dried at $100^\circ C$ in ammonia-free water and dilute to 1,000 ml = 1 ml = 0.1 mg N.

4. Procedure

- 4.1 Add 500 ml distilled water, 10 ml phosphate buffer solution and a few boiling chips to an 800 ml flask and steam out the entire distillation apparatus until the distillate shows no trace of ammonia.
- 4.2 Place a previously prepared acid sample in a 800 ml kjeldahl flask and add 500 ml of ammonia-free distilled water. *Neutralize to about pH 6.6 using a pH meter if necessary then add 10 ml phosphate buffer solution. Add a few boiling chips.

* Boil to remove H_2S , if present.

Ammonia Nitrogen in Bottom Sediments - Distillation

- 4.3 Distillation: Distill over 300 ml at the rate of 6-10 ml/min. collecting the distillate in 50 ml of .02N H_2SO_4 . Place distillate in a glass stoppered 500 ml graduate cylinder and bring up to 500 ml with ammonia free water and mix.
- 4.4 Color Development: Place 50 ml portion of the distillate in a 50 ml nessler tube. Add 1 ml of nessler reagent and mix thoroughly by inverting the tube six times. Allow to stand 20 minutes and read at 425 m μ .
- 4.5 A standard and blank should also be run in the same manner as the sample.

5. Calculation

5.1 Wet Basis:

$$\text{mg/kg} = \frac{\text{mg in Std.} \times \text{O.D. Sample} \times 1000}{\text{O.D. Std.} \left(\frac{\text{g Sample}}{\text{in aliquot}} \right)}$$

5.2 Dry Basis:

$$\text{mg/k} = \frac{\text{mg/kg wet basis}}{\% \text{ Solids (decimal fraction)}}$$

*Boil to remove H_2S if present.

6. Reference

Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965, 191.

NITRATE AND NITRITE NITROGEN IN BOTTOM SEDIMENTS-AUTOANALYZER

32

1. General Discussion

- 1.1 Principle: The nitrate in bottom sediment is reduced to nitrite by passing the sample stream through a ten-inch column of zinc granules (20 mesh) in the presence of sodium acetate and hydrochloric acid buffer. The hydrogen gas is allowed to escape through a T vent. The sample stream is then joined by the color reagent where the nitrite is determined by the formation of a reddish purple azo dye, at a pH 2.0 to 2.5, by coupling of diazotized sulfanilic acid with naphthylamine hydrochloride. The stream then passes through a delay column to allow more time for color development, and then through the colorimeter where the optical density is measured at a wave length of 520 millimicrons.
- 1.2 Interference: See Standard Methods, 12th Edition, 1965, page 205.
- 1.3 Minimum Detectable Concentration: 0.01 mg per liter can be detected with a reasonable degree of precision and accuracy.

2. Apparatus

Technicon Auto-Analyzer, consisting of large sampler, proportioning pump, colorimeter and recorder. See flow diagram in Figure 1.

3. Reagents

- 3.1 Sodium acetate solution M/4: Dissolve 34 g $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ in distilled water and dilute to 1,000 ml.
- 3.2 Sodium acetate hydrochloric acid buffer solution: Mix 100 ml of HCl (1 / 99) with 1,000 ml of sodium acetate solution M/4.
- 3.3 Sulfanilic acid reagent: Completely dissolve 3.0 g of sulfanilic acid in 350 ml hot distilled water, cool, add 100 ml concentrated hydrochloric acid, dilute to 500 ml with distilled water and mix thoroughly.
- 3.4 Naphthylamine hydrochloride reagent: Dissolve 3.0 g naphthylamine hydrochloride in a solution containing 150 ml distilled water, 5 ml concentrated hydrochloric acid and 250 ml of 95% ethyl alcohol. Dilute to 500 ml with distilled water and mix thoroughly.
- 3.5 Color reagent: Mix equal volumes of sulfanilic acid reagent and naphthylamine hydrochloride reagent. Protect from light and refrigerate to increase stability.

Nitrate and Nitrite Nitrogen in Bottom Sediments- Auto-Analyzer

- 3.6 Zinc metal: 20 mesh granular reagent grade; wash with 1 / 99 HCl, rinse with distilled water followed with a rinse of ethyl alcohol, dry and rinse with chloroform.
- 3.7 Stock nitrate solution: Dissolve 7.2180 g anhydrous KNO_3 in distilled water and dilute to 1,000 ml. This solution contains 1.00 mg of nitrate nitrogen per ml.
- 3.8 Lower working standards are prepared from the stock solution. Concentrations dependent upon anticipated levels to be found in sample.

4. Procedure

- 4.1 Place a previously prepared sample into a 200 ml pyrex volumetric flask and add distilled H_2O to approximately half-fill volumetric flask and add 5 or 6 drops of conc. H_2SO_4 .
- 4.2 Boil for 15 minutes to dissolve all nitrates from the sediment and cool.
- 4.3 Centrifuge at 2,000 RPM for 5 or 10 minutes, then decant into volumetric flask. Wash residue with distilled water by thoroughly mixing residue with a stirring rod, follow by centrifuging.
- 4.4 Decant wash solution into volumetric flask and repeat a second time.
- 4.5 Make up to volume with distilled water.
- 4.6 Filter aliquot through membrane filter (having a porosity of 0.45 μ) into test tube.
- 4.7 Place samples in Technicon Auto-Analyzer sampler with one distilled water wash between each sample.
- 4.8 Permit 30 minutes for instrument warm-up and establish a base line.
- 4.9 Set the instrument for two minute sampling time and slightly greater than two minutes for relay time.

Nitrate and Nitrite Nitrogen in Bottom Sediments- Auto-Analyzer

5. Calculation

- 5.1 Mg/l in aliquot may be calculated by comparing peak height of sample with standards, employing a chart reader.

$$\text{wet basis: } \frac{\text{mg/kg}}{\text{mg/l}} = \frac{\text{mg/l in aliquot}}{\text{g/l of sample in sample vol.}} \times \text{Dil. Factor} \times 1000$$

$$\text{dry basis: } \frac{\text{mg/kg}}{\text{mg/kg}} = \frac{\text{mg/kg (wet basis)}}{\% \text{ solids (decimal fraction)}}$$

Nitrite may be determined on the auto-analyzer by by-passing the zinc column and manually according to Standard Methods, 12th Edition, 1965, pages 205-208.

6. References

- 6.1 James E. O'Brien and Janece Fiore Dio of Laboratories and Research, New York State Department of Health
- 6.2 Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965, 205-208.
- 6.3 L. J. Kamphake, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio.
- 6.4 Chemistry of the Soil, ACS Monograph No. 160, 2nd Ed., p. 264 (1964). Reinhold Pub. Co., N.Y.

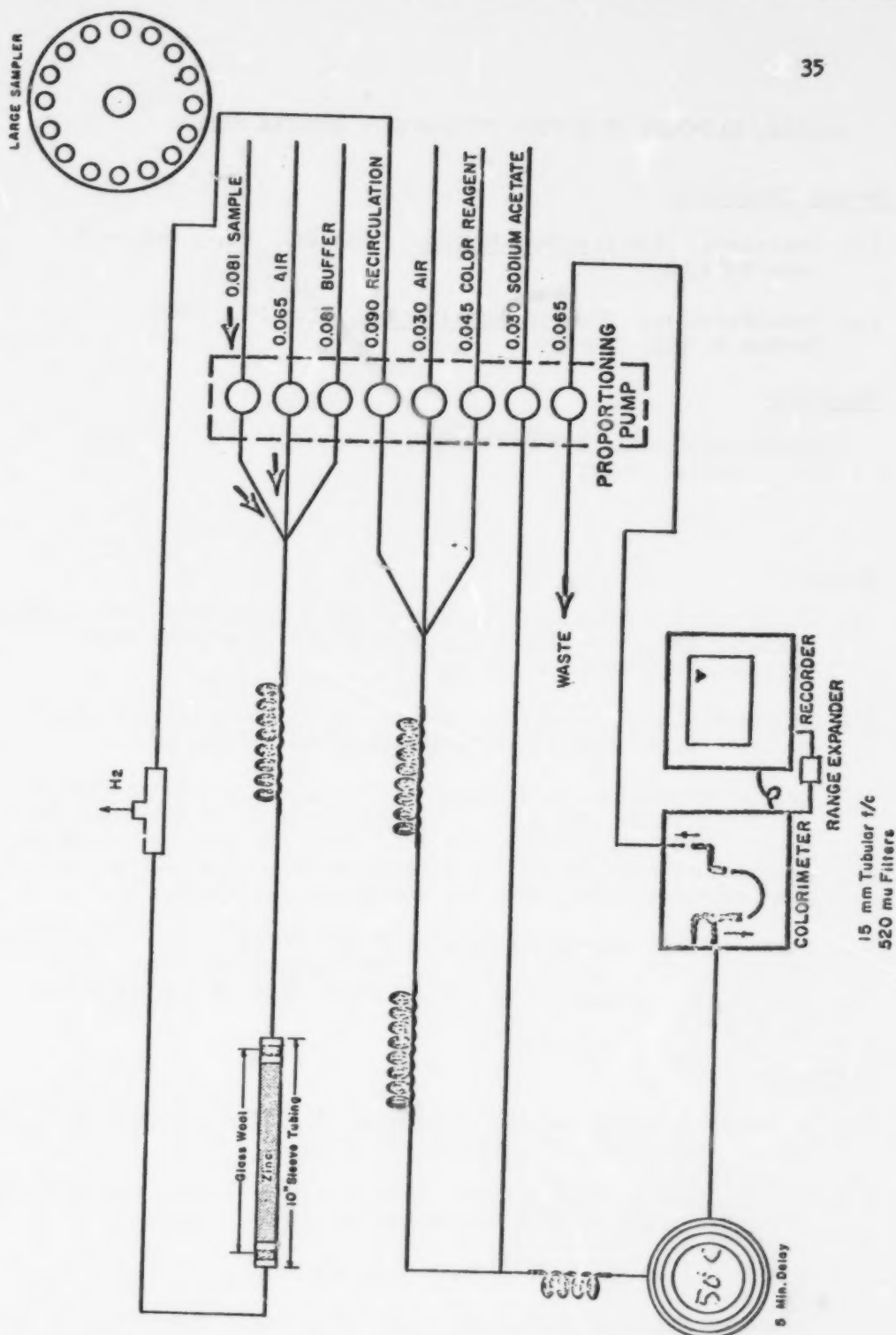


Figure 1

NITRATE NITROGEN IN BOTTOM SEDIMENTS - BRUCINE METHOD

1. General Discussion

- 1.1 Principle: See Standard Methods, 12th Ed., 1965, Method B, page 198-199.
- 1.2 Interferences: See Standard Methods, 12th Ed., 1965, Method B, page 198-199.

2. Apparatus

Spectrophotometer for use at 410 m μ , providing a light path of 1 inch or longer.

3. Reagents

- 3.1 Stock nitrate solution: Dissolve 0.7218 g anhydrous potassium nitrate, KNO₃, and dilute to 1,000 ml with distilled water. This solution contains 100 mg/l N.
- 3.2 Standard nitrate solution: Dilute 100 ml stock nitrate solution to 1,000 ml with distilled water; 1.00 ml = 0.010 mg N.
- 3.3 Brucine-sulfanilic acid reagent: Dissolve 1 g brucine sulfate and 0.1 g sulfanilic acid in approximately 70 ml hot distilled water. Add 3 ml concentrated HCl, cool, and make up to 100 ml. This solution is stable for several months. The pink color that develops slowly does not affect its usefulness.
- 3.4 Sulfuric acid solution: Carefully add 500 ml of conc. H₂SO₄ to 75 ml distilled water. Cool to room temperature before use. Keep tightly stoppered to prevent absorption of atmospheric moisture.

4. Procedure

- 4.1 Transfer a portion of the previously clarified sample = 10 ml to one of the matched 1" colorimetric tubes.
- 4.2 If less than a 10 ml aliquot is taken for analysis, add sufficient distilled water to make the volume 10 ml.
- 4.3 Add 2.0 ml of 30% NaCl to each tube and mix.
- 4.4 Transfer the rack containing these tubes to an ice water bath.

Nitrate Nitrogen in Bottom Sediments - Brucine Method

- 4.5 Add 10 ml of the sulfuric acid solution to each tube (one tube at a time) mix and return to the ice bath. Allow the tubes to reach thermal equilibrium before proceeding to the next step.
- 4.6 Add 0.5 ml of brucine reagent (caution - poison) to each tube, mix thoroughly and return to the rack.
- 4.7 Transfer the rack, with tubes, to a water bath and hold for 20 min. at a temperature just below boiling.
- 4.8 At the end of 20 min. return the rack to the ice bath and cool to room temperature.
- 4.9 Read the absorbance of the sample versus a blank in a spectronic-20, set at 410 mμ within 30 min.
- 4.10 Prepare a calibration curve using standards which were run concurrently with the samples.

5. Calculations

5.1 Wet Basis:

$$\text{mg/kg} = \frac{\text{mg Std}}{\text{OD Std}} \times \frac{\text{OD Sample}}{\text{(grams sample in aliquot)}} \times 1000$$

5.2 Dry Basis:

$$\text{mg/kg} = \frac{\text{mg/kg wet basis}}{\% \text{ Solids (decimal fraction)}}$$

6. References

- 6.1 Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965, 198-199.
- 6.2 Chemical Analysis for Water Quality, A Training Course Manual, U.S. Dept. of Interior, FWPCA, Aug. 1966, pp 13, 11-13, 12.

ORGANIC AND TOTAL KJELDAHL NITROGEN IN BOTTOM SEDIMENTS

Organic nitrogen may be determined by digestion of the sample after removal of free ammonia, with subsequent distillation and titration with standard acid or as the difference between the value obtained for total kjeldahl nitrogen and that for free ammonia.

1. General Discussion

- 1.1 Principle: The kjeldahl method, using mercuric sulfate as a catalyst, converts organically bound nitrogen in the trinegative state to ammonium bisulfate by digestion with sulfuric acid to which potassium sulfate has been added to raise the boiling point to $345^{\circ} - 370^{\circ}\text{C}$. The temperature should not exceed 382°C or loss of nitrogen will result. After dilution, the solution is made alkaline with sodium hydroxide and the ammonia is distilled into $0.2\text{N H}_2\text{SO}_4$ or boric acid solution. If distillate is collected in $0.02\text{N H}_2\text{SO}_4$ acid the ammonia nitrogen should be determined by nesslerization and if distillate is collected in 2% boric acid, the ammonia nitrogen should be determined by titration with $0.02\text{N H}_2\text{SO}_4$, using a mixed indicator.
- 1.2 Interference: In the presence of large quantities of nitrogen-free organic matter, it is necessary to add an additional 50 ml of sulfuric acid-mercuric sulfate-potassium sulfate solution for each gram of solid material in the sample.
- 1.3 Storage: Because organic nitrogen in unsterilized sewage and sludges is continually ammonified, the determination must be made on a freshly collected sample. If the analysis cannot be made at once, the sample must be preserved with sufficient sulfuric acid to obtain a concentration of 1,500 mg/l H_2SO_4 or more (.8 ml/l).

2. Apparatus

- 2.1 Digestion apparatus, provided with a suction take-off to remove water vapor and sulfur trioxide fumes.
- 2.2 Distillation apparatus: See Nitrogen (Ammonia), Standard Methods for the Examination of Water and Wastewater, p. 187-193.

3. Reagents

- 3.1 Ammonia-free water

Organic and Total Kjeldahl Nitrogen in Bottom Sediments

- 3.2 Sodium Sulfate (low in nitrogen).
 - 3.3 Mercuric Sulfate.
 - 3.4 Litmus Paper.
 - 3.5 Sodium hydroxide-sodium thiosulfate solution: Dissolve 500 g NaOH and 25 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in distilled water and dilute to 1 liter.
 - 3.6 Phenolphthalein indicator solution: Either the aqueous (a) or alcoholic (b) solution may be used.
 - a. Dissolve 5 g phenolphthalein disodium salt in distilled water and dilute to 1 liter. If necessary, add 0.02N NaOH dropwise until a faint pink color appears.
 - b. Dissolve 5 g phenolphthalein in 500 ml 95 per cent ethyl alcohol or isopropyl alcohol and add 500 ml distilled water. Then add 0.02N NaOH dropwise until a faint pink color appears.
 - 3.7 Mixed indicator: Mix 2 volumes of 0.2 per cent methyl red in 95 per cent alcohol with 1 volume of 0.2 per cent methylene blue in 95 per cent ethyl alcohol. This solution must be made fresh every 30 days.
 - 3.8 Standard sulfuric acid titrant, 0.02N. In this strength, 1.00 ml = 0.28 mg N. Other strengths of standard acid may be used.
 - 3.9 Sulfuric acid, conc.
 - 3.10 Dissolve 20 g anhydrous boric acid, H_3BO_3 , in ammonia-free water and dilute to 1 liter.
 - 3.11 Antifoam.
4. Procedure
- 4.1 Take either the residue from the free ammonia analysis for organic nitrogen or a new sample for total kjeldahl nitrogen (1 or 2 g).
 - 4.2 Add 35 ml of conc. H_2SO_4 plus 15 g Na_2SO_4 , plus 3 g mercuric sulfate and a little antifoam and allow to boil until white fumes appear.

Organic and Total Kjeldahl Nitrogen in Bottom Sediments

- 4.3 After fumes appear, allow to digest for 30 minutes turning the flask from time to time. Cool to room temperature.
- 4.4 To cooled sample, add 500 ml of ammonia-free water, 0.3 ml (1 dropper full) of phenolphthalein or litmus paper, and then add 50 to 75 ml of 50% NaOH-thiosulfate solution being careful not to mix. Place on distillation rack and mix. If the solution is not red or litmus paper is not blue, add more NaOH until a red color appears or litmus is blue.
- 4.5 Distill over 300 ml collecting the distillate in 50 ml of 2% boric acid. To this add 10 drops of mixed indicator and titrate with 0.02N H_2SO_4 which has been standardized against 0.02N Na_2CO_3 .
- 4.6 Blanks and standards should be run in the same manner as the samples.

5. Calculation

5.1 Wet basis (titration)

$$\text{mg/kg} = \frac{\text{ml of } 0.02 \text{ } NH_2SO_4 \times 0.28}{\text{g sample}} \times 1000$$

5.2 Dry basis

$$\text{mg/kg} = \frac{\text{mg/kg wet basis}}{\% \text{ Solids (decimal fraction)}}$$

5.3 Wet basis (colorimetric)

$$\text{mg/kg} = \frac{\text{mg in Std} \times \text{O.D. Sample} \times 1000}{\text{O.D. Std} \left(\frac{\text{g Sample}}{\text{in aliquot}} \right)}$$

5.4 Dry basis

$$\text{mg/kg} = \frac{\text{mg/kg wet basis}}{\% \text{ solids (decimal fraction)}}$$

6. Nitrogen (Total Kjeldahl) - (Bottom Sediments)

Total kjeldahl nitrogen includes ammonia and organic nitrogen, but does not include nitrite and nitrate nitrogen. The method is the same as that for organic nitrogen, except that the ammonia removal step is omitted. The procedure therefore begins with Sec.4. Place an appropriate aliquot of a well-mixed sample in an 800-ml kjeldahl flask. (1 or 2 g)

Organic and Total Kjeldahl Nitrogen in Bottom Sediments

7. Reference

Standard Methods for the Examination of Water and Wastewater,
12th ed., APHA, Inc., N.Y., 1965, 187-193.

OIL AND GREASE IN BOTTOM SEDIMENTS

1. General Discussion

- 2.1 Definition: Grease is defined as that material extracted by hexane from an acidified sample which would not be volatilized during the procedure; it includes soaps, fats, waxes, and oils.
- 1.2 Principle: Drying of acidified sludges by heating leads to low results. Magnesium sulfate monohydrate is capable of combining 75 per cent of its own weight in water in forming the heptahydrate. Magnesium sulfate monohydrate can be used to dry sludge. After drying, the grease can be extracted with hexane.
- 1.3 Interference: Elemental sulfur; certain organic dyes; oxidation of extract and loss in weight of residue due to volatilization of low boiling components.
- 1.4 Sampling and Storage: Every possible precaution must be taken to obtain a representative sample. When analyses can not be made immediately, samples may be preserved with 1 ml conc H_2SO_4 for each 80 g of sample, or by freezing.

2. Apparatus

- 2.1 Extraction apparatus, soxhlet or A.S.T.M. apparatus.

3. Reagents

- 3.1 Hydrochloric acid conc.
- 3.2 Magnesium sulfate monohydrate: Prepare $\text{Mg SO}_4 \cdot \text{H}_2\text{O}$ by drying overnight a thin layer of $\text{Mg SO}_4 \cdot 7\text{H}_2\text{O}$ in an oven at 103°C .
- 3.3 N-Hexane, boiling point 69°C .
- 3.4 Grease free cotton: Nonabsorbent cotton after extraction with N-hexane.

4. Procedure

- 4.1 In a 150 ml beaker weigh a 20 g sample of wet sludge, of which the dry-solids content is known.
- 4.2 Acidify to a pH 2.0 (generally 0.3 ml conc HCl is sufficient).

Oil and Grease in Bottom Sediments

- 4.3 Add 25 g magnesium sulfate monohydrate. Stir to a smooth paste and spread on the sides of the beaker to facilitate subsequent moisture removal. Allow to stand until solidified 15 to 30 minutes.
- 4.4 Remove the solids and grind in a porcelain mortar.
- 4.5 Add the powder to a paper extraction thimble. Wipe the beaker and mortar with small pieces of filter paper moistened with hexane and add to the thimble. Fill the thimble with small glass beads.
- 4.6 Extract in a soxhlet apparatus using hexane at a rate of 20 cycles per hour for 4 hours.
- 4.7 If any turbidity or suspended matter is present in the extraction flask, remove by filtering through grease-free cotton into another weighed flask. Rinse flask and cotton with hexane.
- 4.8 Distill hexane from the extraction flask in water at 85°C. Dry by placing on a steam bath and drawing air through the flask with a vacuum for 15 minutes.
- 4.9 Cool in a desiccator for 30 minutes and weigh.

5. Calculation

5.1 Wet basis

$$\text{mg/kg} = \frac{\text{mg of residue}}{\text{grams of sample}} \times 1000$$

5.2 Dry basis

$$\text{mg/kg} = \frac{\text{mg/kg wet basis}}{\% \text{ solids (decimal fraction)}}$$

6. Reference

Standard Methods for the Examination of Water and Wastewater,
12th Ed., APHA, Inc., N.Y., 1965, 531-532.

IMMEDIATE DISSOLVED OXYGEN DEMAND AND BIOCHEMICAL OXYGEN DEMAND
OF BOTTOM SEDIMENTS

1. General Discussion

- 1.1 See Standard Methods for the Examination of Water and Waste-Water, 12th Edition, page 415.
- 1.2 The extremely high dilutions used will help to minimize any interferences due to toxic materials.

2. Apparatus

- 2.1 Incubation bottles, 300 ml bottles with water seal. Ground-glass stoppered bottles should be cleaned with a good detergent or dichromate cleaning solution and thoroughly rinsed with distilled H_2O and drained. Satisfactory water seals are obtained by adding water to the top of the BOD bottles each morning.
- 2.2 Air incubator, thermostatically controlled at $20^{\circ}C \pm 1^{\circ}C$ (All light should be excluded to prevent formation of DO by algae in the sample.)

3. Reagents

- 3.1 Distilled water used for solutions and for preparation of the dilution water must be of the highest quality, distilled from a block tin or all-glass still, contain less than 0.01 mg/l copper, and be free of chlorine, chloramines, caustic alkalinity, organic material, or acids and have a specific resistance of 750,000 OHMS or higher. The distilled water used for dilution water should be aged or stabilized in the dark for 30 days prior to using it.
- 3.2 Phosphate buffer solution: Dissolve 8.5 g potassium dihydrogen phosphate, KH_2PO_4 ; 21.75 g dipotassium hydrogen phosphate, K_2HPO_4 ; 33.4 g disodium hydrogen phosphate heptahydrate, $Na_2HPO_4 \cdot 7H_2O$ and 1.7 g ammonium chloride, NH_4Cl , in about 500 ml distilled water and dilute to 1 liter. The pH of this buffer should be 7.2.
- 3.3 Magnesium sulfate solution: Dissolve 22.5 g $MgSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 liter.
- 3.4 Calcium chloride solution: Dissolve 27.5 g $CaCl_2$ in distilled water and dilute to 1 liter.
- 3.5 Ferric chloride solution: Dissolve 0.25 g of $FeCl_3 \cdot 6H_2O$ in distilled water and dilute to 1 liter.

Immediate Dissolved Oxygen Demand and Biochemical Oxygen Demand of
Bottom Sediments

- 3.6 BOD standard: Dissolve 0.150 g each of reagent grade glucose and glutamic acid which have been dried at 103°C for 1 hour in distilled water and dilute to 1 liter.
- 3.7 Seeding material: A satisfactory seed may be obtained by using the supernatant liquor from raw domestic sewage which has been stored at 20°C for 24 hours.

4. Procedure

- 4.1 Preparation of dilution water: The distilled water used should have been aged in cotton-plugged bottles for a sufficient length of time to insure stabilization and to give blank depletions of not more than 0.2 mg, preferably 0.1 mg, oxygen. Usually 30 days are required. The water should be aerated just prior to use to insure saturation at 20°C. Add 1 ml each of phosphate buffer, magnesium sulfate, calcium chloride, and ferric chloride solutions for each liter of dilution water.
- 4.2 Seeding: Add proper amount of seed (to give 2 mg/l depletion), which has been filtered through two thicknesses of Kimwipes for each liter of water. The amount of seed required may vary with the source of seed and will have to be established through experience.
- 4.3 Weigh appropriate size sample directly into the BOD bottle, suggested weight 6 grams.
- 4.4 Fill BOD bottle with dilution water and place in incubator.
- 4.5 Make sure that there is a water seal in the neck of each bottle when placed in the incubator. Each morning replenish the water seal on all bottles.
- 4.6 Determination of initial DO: Determine the initial DO of the dilution water by means of the azide modification of the iodometric method. This DO value is used as the initial DO of the sample. This method is used because it is not possible to obtain an exact initial DO of the bottom sediment due to the rapid consumption of oxygen.
(a) If a DO probe is used, IDOD and BOD can be run on the same bottle.
- 4.7 Incubation: Incubate the blank (dilution water) and the diluted samples for 5 days at 20°C. Then determine the DO in the incubated samples using the above methods. Those dilutions showing a residual DO of 2 mg/l and a depletion of 2 mg/l are considered the most reliable.
- 4.8 Dilution water control: Fill two BOD bottles with unseeded dilution water. Stopper and water-seal one of these for incubation. The other bottle is for determining DO prior to incubation. The DO results on these two bottles are used as a check on the quality of the unseeded dilution water. The depletion obtained should not be more than 0.2 ml and preferably not more than 0.1 ml.

4.9 Glucose-glutamic acid check: To check the dilution water, the seed material and the technique of the analyst, make up a two percent dilution of the primary BOD standard. Fill three bottles and incubate at 20°C for 5 days. A two percent dilution of the BOD standard solution should give a BOD of 218 mg/l with a standard deviation of + 21 mg/l. If the results deviate from this value appreciably, the quality of the seed, water and the technique is questionable.

5. Immediate Dissolved Oxygen Demand

5.1 This test is carried out in the same manner as the 5-day BOD test, except that the sample is held for only 15 minutes and the DO is determined.

5.2 Calculation:

Wet basis

$$\text{I DOD mg/kg} = \frac{(D_0 - D_1) \times 0.3}{\text{grams of sample in aliquot}} \times 1000$$

Dry basis

$$\text{I DOD mg/kg} = \frac{\text{mg/kg I DOD (wet basis)}}{\% \text{ solids (decimal fraction)}}$$

6. BOD Calculation

6.1 Wet basis

$$\text{mg/kg} = \frac{(D_0 - D_2) \times 0.3}{\text{grams of sample in aliquot}} \times 1000$$

6.2 Dry basis

$$\text{mg/kg} = \frac{\text{mg/kg (wet basis)}}{\% \text{ solids (decimal fraction)}}$$

6.3 Definitions

D_0 = DO of original dilution water.

D_1 = DO of diluted sample 15 min. after preparation.

D_2 = DO of diluted sample after incubation (after 5 days).

7. Reference

Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965, 415.

OXYGEN UPTAKE OF BOTTOM SEDIMENTS

1. General Discussion

The oxygen demand of bottom sediments is a complex phenomenon occurring at the water-sediment interface, where chemical and biochemical oxidation and reduction reactions take place at various rates depending upon conditions existing at a particular time.

Since bottom sediments tend to be of a reducing character, water flowing over these sediments lose oxygen to the sediment interface, which becomes an oxidized microzone of ferric oxide. Under these conditions, the water-sediment interface is a brown color and the radox potential in this system is greater than 0.2 volts. When stagnation progresses and conditions become anaerobic, the radox potential is less than 0.2 volts and the brown color disappears.

The presence or absence of the oxidized microzone makes an immense difference in the amount and nature of materials that are leached from these sediments and the rate of oxygen uptake from the waters above.

The amount of oxygen consumed by bottom sediments is often great enough so that it causes the overlying waters to become void of oxygen several feet above the water-sediment interface. Therefore, it is important to know the characteristics of these bottom sediments and their oxygen uptake rates.

2. Apparatus

- 2.1 Laboratory Oxygen Analyzer.
- 2.2 Magnetic Stirrer with one-inch teflon coated magnets.
- 2.3 Incubator, 20°C.
- 2.4 Wide-mouth Cylindrical Jars with screw cap and sealed probe; minimum mouth opening of 11 cm; height 25 cm; for use in making O₂ uptake apparatus (see attached diagram).
- 2.5 Glass Petri Dish with cover.
- 2.6 Glass Petri Dish Support.
- 2.7 Asbestos Sheet, 15 x 15 x 0.5 cm.

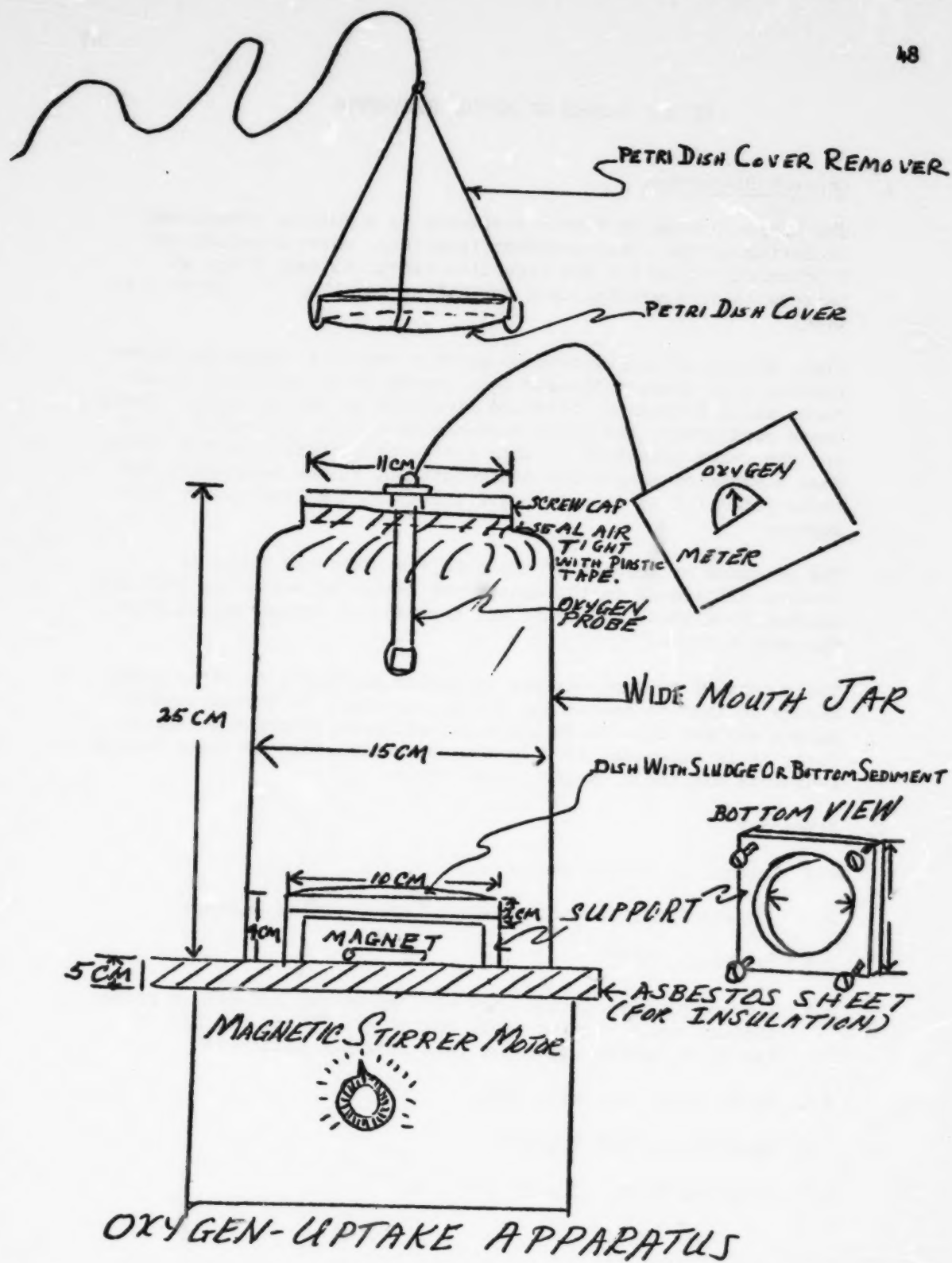


Figure No. 1

3. Reagents

- 3.1 Distilled water: Water used for solutions and for preparation of the dilution water must be of the highest quality, distilled from a block tin or all-glass still, contain less than 0.01 mg/l copper, and be free of chlorine, chloramines, caustic alkalinity, organic material, or acids.
- 3.2 Phosphate buffer solution: Dissolve 8.5 g potassium dihydrogen phosphate, KH_2PO_4 ; 21.75 g dipotassium hydrogen phosphate, K_2HPO_4 ; 33.4 g disodium hydrogen phosphate heptahydrate, $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, and 1.75 g ammonium chloride, NH_4Cl , in about 500 ml distilled water and dilute to 1 liter. The pH of this buffer should be 7.2 without further adjustment. If dilution water is to be stored in the incubator, the phosphate buffer should be added just prior to using the dilution water.
- 3.3 Magnesium sulfate solution: Dissolve 22.5 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water and dilute to 1 liter.
- 3.4 Calcium chloride solution: Dissolve 27.5 g anhydrous CaCl_2 in distilled water and dilute to 1 liter.
- 3.5 Ferric chloride solution: Dissolve 0.25 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in distilled water and dilute to 1 liter.
- 3.6 Acid and alkali solutions, 1N. For neutralization of waste samples which are either caustic or acidic.
- 3.7 Sodium sulfite solution, 0.025N. Dissolve 1.575 g anhydrous Na_2SO_3 in 1,000 ml distilled water. This solution is not stable and should be prepared daily.
- 3.8 Seeding material: A satisfactory seed may be obtained by using the supernatant liquor from raw domestic sewage which has been stored at 20°C for 24 hours.

4. Procedure

- 4.1 Preparation of dilution water: The distilled water used should have been stored in cotton-plugged bottles for a sufficient length of time to become saturated with DO. The water may also be aerated by shaking a partially filled bottle or with a supply of clean compressed air. Situations may be encountered where it is desired to use stabilized river water to check stream performance with laboratory procedure. The distilled water used should be as near 20°C as possible and of the highest purity. Place the desired volume of distilled water in a suitable bottle and add 1 ml each of phosphate buffer, magnesium sulfate, calcium chloride, and ferric chloride solutions for each liter of water.

Oxygen Uptake of Bottom Sediments

- 4.2 Place a covered petri dish containing a weighed amount of well-mixed sediment in place, as shown in the sketch of oxygen uptake apparatus.
- 4.3 Fill the jar with dilution water, measuring volume of added water, then remove the petri dish cover.
- 4.4 Insert oxygen probe with cap after standardizing probe against Winkler DO method, following the manufacturer's manual and place sample in a 20°C incubator.
- 4.5 Seal system and with magnetic stirrer set to give approximately the same flow occurring in the lake or streams. Take dissolved oxygen readings at various time intervals. In general, time intervals of 0, 0.5, 1, 2, 3, 4, 5, 6, 8, 10, 15, 20 and 30 days are satisfactory. The frequency of readings is dependent upon the rate of oxygen uptake.

5. Calculation of oxygen uptake

Wet basis

$$\frac{A \times 1000}{B} = \text{mg/kg}$$

Dry basis

$$\text{mg/kg} = \frac{\text{mg/kg wet basis}}{\% \text{ solids (decimal fraction)}}$$

A = Initial reading - Final reading

B = Weight of sample in grams per liter

Oxygen uptake may be calculated on the basis of weight or unit area by substituting surface area of sediment exposed to the dilution water in place of B (the weight of sediment) in the above formula.

6. Calculation of K_1 values

- 6.1 From the 5-day BOD values (y), calculate the daily differences as shown below:

t	O ₂ -demand	Differences
0		
0.5		
1	0.72	0.72
1.5		0.48
2	1.20	
2.5		0.35
3	1.55	
3.5		0.27
4	1.82	
4.5		0.20
5	2.02	

Oxygen Uptake of Bottom Sediments

- 6.2 Plot the differences on semi-log paper with differences on the log scale and time on linear scale. The time coordinates are 0.5, 1.5, 2.5, etc.
- 6.3 Draw a straight line through the points, extending the line to $t = 0$ (left margin).
- 6.4 Determine the slope of this line by using values at 5 days and 0 days.

5 days = 0.175 and 0 days = 0.74.

$$\frac{0.175}{0.74} = 0.237$$

Slope X 100 = % remaining in 5 days = 23.7%

- 6.5 Using the formula, $\log \% \text{ BOD remaining} = 2.0 - K_1 t$; K_1 can be calculated as follows:

$$\begin{array}{rcl} \log & 23.7 & = 2.0 - K_1 5 \\ & 1.374 & = 2.0 - K_1 5 \\ & K_1 & = \frac{2.0 - 1.374}{5} \end{array}$$

$$K_1 = 0.13$$

- 6.6 The formula $Y = L (1 - 10^{-K_1 t})$ and the above data will permit the calculation of L , L being the ultimate BOD, Y the 5-day BOD, and $(1 - 10^{-K_1 t})$ the fraction oxidized.

Fractions oxidized = 1 - fraction remaining

$$= 1 - 0.237$$

$$= 0.763$$

Therefore $2.02 = L \times 0.763$

$$L = \frac{2.02}{0.763}$$

$$L = 2.7 \text{ mg/l}$$

7. References

- 7.1 Sheehy, J. P. "Rapid Methods for Solving Monomolecular Equations," J.W.P.C.F., 32:646, June 1960.
- 7.2 Moments Methods: Moore, E.W., Thomas, H.A., and Snow, W.B., "Simplified Method for Analysis of BOD Data," Sewage and Industrial Wastes, 22: 10, 1950.
- 7.3 Tsivoglou, E.C., "Oxygen Relationships in Streams," Technical Report W-58-2, Robert A. Taft Sanitary Engineering Center, 1958.
- 7.4 Muhlman, F.W., "Oxygen Demand of Sludge Deposits," J. Sewage Works, 10, 613 (1938).
- 7.5 Rudolfs, Willem, "Relation between Biochemical Oxygen Demand and Volatile Solids of Sludge Deposits in the Connecticut River. J. Sewage Works, 4, 317 (1932).
- 7.6 Beckman Instructions #1223, Beckman Instruments, Inc. (1962).

CHLORINE DEMAND OF BOTTOM SEDIMENTS

1. General Discussion

"The chlorine demand of a water is caused by such inorganic reductants as ferrous, manganous, nitrite, sulfide, and sulfite ions. Ammonia and cyanide consume considerable chlorine during the free residual chlorination process. Chlorine substitutes on phenols and other similar aromatic compounds to form chloro derivative compounds, but may also oxidize the aromatic compounds when larger amounts of chlorine are added. It may also react with ammonia and naturally occurring amino compounds to form chloramines with an active or oxidizing chlorine atom. The destruction of the chloramine compounds can be achieved by the addition of more chlorine and subsequently with the addition of enough chlorine a free available residual (hypochlorous acid) may be attained.

"The chlorine demand of water is the difference between the amount of chlorine applied to a treated supply and the amount of free, combined, or total available chlorine remaining at the end of the contact period. The chlorine demand of any given water varies with the amount of chlorine applied, time of contact, pH, and temperature. For comparative purposes it is imperative that all test conditions be stated. The smallest amount of residual chlorine considered significant is 0.1 mg/l Cl. Presented here is a method for laboratory use and a field procedure which gives less exact results.

1.1 Principle:

The laboratory method is designed to determine the so-called immediate demand as well as other demands at longer contact periods. Chlorine demand determinations are made to determine the amount of chlorine that must be applied to a water to produce a specific free, combined, or total available chlorine residual after a selected period of contact. If the amount of chlorine applied to waters containing ammonium or organic nitrogen compounds is not sufficient to reach what is termed the "breakpoint" chloramines and certain other chloro derivatives which react as combined available residual chlorine are produced. When sufficient chlorine has been added to reach the breakpoint, which depends on pH, ratio of chlorine to nitrogenous compounds present, and other factors, subsequent additions of chlorine remain in the free available state." (Standard Methods, 12th Edition, pp.112-113)

Chlorine Demand of Bottom Sediments

2. Reagents

- 2.1 Acetic acid, conc.
- 2.2 Potassium iodide, crystals.
- 2.3 Standard thiosulfate, 0.037 N.
- 2.4 Solution of starch, 5 grams of starch per liter of water.
- 2.5 Chlorine solution adjusted so that 1 ml contains approximately 1 mg of chlorine.
- 2.6 Aged distilled chlorine free water.

3. Apparatus

- 3.1 Stirrer and magnetic stirring bars.
- 3.2 500 ml erlenmeyer flasks.
- 3.3 50 ml buret.
- 3.4 Aluminum foil.

4. Procedure

- 4.1 Weigh 1-2 grams of well-mixed bottom sediment onto prepared aluminum strips.
- 4.2 Wash sediment from aluminum strips into an erlenmeyer flask containing 200 ml of aged chlorine free water by moving aluminum strip up and down below surface in flask.
- 4.3 Pipet 20 ml of standardized chlorine solution into sample with rapid stirring to insure instantaneous mixing and then stir slowly in darkness for exactly 15 minutes.
- 4.4 Add 5 ml of acetic acid, approximately 1 gram of potassium iodide, 1 to 2 ml of starch solution and titrate with 0.0370 N thiosulfate to the point of disappearance of the blue color. Note - it is necessary to add the starch at the beginning of the titration due to the difficulty in detecting the end point in the presence of turbidity produced by the sediment.

Chlorine Demand of Bottom Sediments

5. Calculation

One ml of 0.037 N thiosulfate is equivalent to 1.3010 mg chlorine.

5.1 Wet Basis:

$$\text{mg/kg Cl demand} = \frac{\text{mg Cl added} - \text{mg Cl residual}}{\text{Wt of sediment}} \times 1000$$

5.2 Dry Basis:

$$\text{mg/kg} = \frac{\text{mg/kg wet basis}}{\% \text{ Solids (decimal fraction)}}$$

6. Reference

Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965, 112-113.

PESTICIDES IN BOTTOM SEDIMENTS

Preparation of Sample

1. General Discussion

- 1.1 Principle: Pesticides sorbed on particulate matter may be desorbed by the continuous Soxhlet Extraction of a ground and dried bottom sediment sample with suitable organic solvent(s). The extract containing the pesticide(s) is cleaned up and analyzed by gas chromatography, thin layer chromatography, and infrared spectroscopy.

2. Apparatus

- 2.1 Soxhlet extractor, flask capacity (500 ml), with Allihn condenser.
- 2.2 Extraction thimbles, Whatman single thickness, 43 x 123 mm or a convenient size.
- 2.3 Chromatographic tube 20 x 400 mm.
- 2.4 Thin layer chromatography equipment.
- 2.5 Gas chromatograph equipped with microcoulometric titration cells.

3. Reagents

- 3.1 Hexane, redistilled in glass b.p. 68° - 69°C.
- 3.2 Ethyl ether, redistilled in glass b.p. 34° - 35°C.
- 3.3 Chloroform, redistilled in glass b.p. 60° - 61°C.
- 3.4 6 parts ethyl ether and 94 parts hexane.
- 3.5 15 parts ethyl ether and 85 parts hexane.
- 3.6 30 parts ethyl ether and 70 parts hexane.
- 3.7 50 parts ethyl ether and 50 parts hexane.
- 3.8 Florisil 60-100 mesh commercial products of this grade may be reactivated by heating 5 hours at 130°C.

Pesticides in Bottom Sediments, Preparation of Sample

4. Procedure

4.1 Preparation for Extraction

- a. Allow the bottom sediment sample to dry thoroughly at room temperature for about a week or cover samples with open mesh cheesecloth and accelerate moisture removal employing a cooling fan. This is best accomplished by breaking up the large particles and spreading out in a glass dish or aluminum foil.
- b. Grind up sample with a mortar and pestle and pass it through a 30 mesh sieve.
- c. Select a 100 g aliquot and place in a pre-extracted thimble. Place a small wad of pre-extracted glass wool or cotton on top of the sample.

4.2 Soxhlet Extraction

- a. Using 300 ml chloroform, extract bottom sediment sample for 18 hours (at 60°C).
- b. Transfer extract to 250 ml beaker and concentrate on a steam bath to about 10 ml; add one drop 0.005% paraffin oil in hexane prior to evaporation.

4.3 Wet Extraction Procedure

Extraction of soils and bottom sediments. Weigh a 100g sample into a liter erlenmeyer flask. Add distilled water to effect a slurry. Add 2 ml of extraction solvent (hexane/IPA, 3:1) per gram of sample and shake vigorously for 20 minutes using a wrist action shaker or equivalent. Decant and collect the hexane phase into a separatory funnel. Repeat extraction of the bottom sediment/aqueous phase two more times quantitatively decanting the hexane portions each time into the separatory funnel. Wash any remaining alcohol from combined hexane extracts with water, dry over sodium sulfate, and concentrate to an appropriate volume.

Pesticides in Bottom Sediments, Preparation of Sample

4.4 Column Chromatography

- a. Prepare a five inch column with 3/4" at top and 1/2" at bottom anhydrous sodium sulfate plus 15 gram Florisil which has been activated 5 hours at 130°C and stored in a desiccator to cool; or for samples containing large quantities of waxes and pigments, use a column containing a mixture of Nuchar C-190 (5g) plus Celite (10 grams). Column may be reduced to 3/8" diameter x 12" (made from glass tubing drawn to approximately 1/16" tip) packed with 1/2" x 1/2" glass wool; reagents must be reduced by a factor of 10.
- b. Pre-wet the column with 50 ml of hexane.
- c. Place the extract on the column and elute into a 200 ml volumetric flask with 200 ml 6%, 15% and 30% or 50% ethyl ether in hexane.
- d. Concentrate the sample from step c to approximately 5 ml in a 250 ml beaker; then transfer to a 15 ml centrifuge tube and concentrate to a volume of 0.1 to 1 ml.
- e. The following pesticides are eluted by the above mixtures of ethyl ether and hexane.

ETHYL ETHER IN HEXANE6%

Lindane
 BHC
 Kelthane
 Aldrin
 Heptachlor
 DDE
 TDE (DDD)
 DDT
 Perthane
 Heptachlor or epoxide
 Methoxychlor
 Toxaphene
 Strobane
 Chlordane
 Endosulfan I

15%

Dieldrin
 Endrin
 Endosulfan II
 Lindane
 Kelthane (possible
 trace of total)

30% or 50%

Generally elute
 Thiophosphate Pesticides

 50% E. Ether elutes
 Guthion

PESTICIDES IN BOTTOM SEDIMENTS

Gas Chromatography with Electron Capture

1. Nonpolar Column

1.1 General Discussion: This procedure is applicable to the analysis of most chlorinated hydrocarbons, a number of esters of the phenoxy-alkanoic acid herbicides, and a few organic phosphates.

1.2 Apparatus:

- a. Gas chromatograph equipped with dual glass columns and electron capture detector, spare electron capture detector recommended.
- b. Strip chart recorder -- 1 mv.
- c. Microsyringes--10- and 50 μ l capacity.
- d. Glass Columns: Non-Polar 6 feet by 1/4" O.D. packed with Gas Chrom Q 60/80 mesh, coated with 5% by weight of OV-17.
- e. Nitrogen tank equipped with regulator valve and tubing to connect with gas chromatograph.

1.3 Reagents:

- a. Stock pesticide standards are made to contain 1 μ g/ml of lindane; heptachlor; aldrin; dieldrin; endrin; o,p-DDT; p,p'-DDT; DDD, DDE, methachlor, and chlordane in hexane.
- b. Pesticide working standards - Pesticide stock standards are diluted with hexane to give the following concentrations:

<u>Standard 1</u>		<u>Standard 2</u>		<u>Standard 3</u>	
	<u>ng/μl</u>		<u>ng/μl</u>		<u>ng/μl</u>
Lindane	0.5	Dieldrin	3.0	Chlordane	10.0
Heptachlor	1.0	Endrin	8.0	Methoxychlor	10.0
Aldrin	1.0				
DDE	7.0				
o, p-DDT	8.0				
p, p'-DDT	8.0				

Pesticides in Bottom Sediments, Gas Chromatography with Electron Capture

1.4 Column Conditioning:

- a. Install the packed column in the gas chromatograph without connecting to the detector device. Heat the column to 270°C without gas flow for two hours. Allow the column to cool to 225°C and maintain this temperature for 10 minutes; then adjust carrier gas to about 50 ml per minute. After one hour, increase column temperature to 240°C and condition the column for 24-48 hours. Cool the column down to operating temperatures 180-215°C and hook up to the detector system. Columns prepared and conditioned in the prescribed manner should yield good chromatograms without major losses of heptachlor or DDT with no further treatment. Even with the most advanced equipment, the analyst is reminded that the system can be no better than the condition of the column. Injection of samples which have not been adequately prepared will undoubtedly shorten the life of the column and yield poor quality chromatograms.
- b. Conditioning of the column can also be done in a separate oven capable of maintaining temperatures up to 270°C and equipped to maintain a flow of carrier gas through the column. This permits conditioning of a standby column while the instrument is being used for residue analysis.
- c. At the end of the preliminary conditioning period, the chromatographic system should be evaluated using pesticide mixtures and standards injected singly. Recovery of chlorinated hydrocarbons should be 75% or higher, and peak shapes should be symmetrical. Evaluation of the chromatographic column can also be done by using the pesticide endrin as a guide. It has been shown that columns not properly conditioned give two peaks for this pesticide at low temperatures owing to catalytic decomposition, but, upon further conditioning, it will give only one peak. Double peaks, however, still can be obtained at high temperatures as a result of thermal decomposition. Individual laboratories must judge whether or not the chromatographic column is operating at maximum efficiency. Before the column is ready for residue analysis, it should give high recoveries of most pesticide standards, good resolution, and symmetrical peaks.

Pesticides in Bottom Sediments, Gas Chromatography with Electron Capture

- d. If further conditioning of the column is indicated, the column should be heat-conditioned for an additional twenty-four hours before reevaluation. It may also be necessary to make several injections of 25 μ l each of the strong pesticide mixture. This should be followed up with several injections of 5 μ l each of the moderate pesticide mixture; if this still does not give a satisfactory chromatogram, injection of purified sample extracts may be necessary. If these materials are available, it is recommended that several 10 μ l injections be made in an attempt to condition the column for residue analysis.
- e. Once a column has been properly conditioned and is ready for residue analysis, it may be necessary to make several injections of the standard pesticide mixture each morning prior to running sample extracts.

1.5 Procedure:

- a. After the nonpolar column has been thoroughly conditioned as described in Section 1.4, on conditioning of the column, it is ready for use. The operating parameters for this column are as follows: column temperature, 195°C; injection block, 230°C; electron capture detector, 200°C; the flow rate of nitrogen through the column is maintained at 120 ml/min., or other optimum conditions.
- b. Optimum operating conditions for the electron capture detector must be determined in the individual laboratory by varying the voltage applied to the detector to find a region where sensitivity is good and response is linear.
- c. For the operation of the gas chromatograph, follow instructions in the manufacturer's manual.
- d. To obtain relative retention times on this column using the electron capture detector, individual pesticides, mixtures (containing aldrin), and unknowns should be injected at the 1 to 10 ng level.
- e. Relative Retention Time (R.R.T.) =
$$\frac{\text{Pesticide's Actual Retention Time in Minutes}}{\text{Actual Retention Time of Aldrin in Minutes}}$$

(Sulphenone is usually the referenced pesticide when computing R.R.T. of thiophosphate pesticides.)

Pesticides in Bottom Sediments, Gas Chromatography with Electron Capture

2. On the Polar Column

- 2.1 General Discussion: This procedure is applicable to the analysis of chlorinated hydrocarbons, a few organic phosphates and some of the phenoxyalkanoic acids and their esters. This column has been selected to give a different pattern of separation of the pesticide standards in order to facilitate identification.
- 2.2 Apparatus:
 - a. (Same as for nonpolar column except the column)
 - b. Glass columns - 6 feet in length by 1/4" O.D. packed with Gas Chrom Q 60/80 mesh coated with 5% QF-1 plus 3% DC-200.
- 2.3 Reagents: (Same as given for non-polar column)
- 2.4 Column Conditioning: (Same as for nonpolar column)
- 2.5 Procedure:
 - a. The operating conditions for the polar column are as follows: column temperature, 180°C; injection block, 230°C; detector, 200°C; flow rate of nitrogen at 100 ml/min. The optimum operating voltage for the direct current mode of operation of the electron capture detector should be determined by injecting a standard solution of lindane and adjusting the voltage until maximum sensitivity and a linear response is obtained. If the two are not compatible, a voltage is chosen that will yield a linear response in the range of 1-10 ng of standards. Then make unknown sample injections in the same manner as standards.
 - b. The polar column should be used to assist in identification of unknown compounds chromatographed on the nonpolar column. This type of confirmation is of great importance when using the electron capture method since some non-pesticide impurities in sample extracts give high responses with this detector.

3. Calculations

Employ the calculations given under Microcoulometric Section - "Measurement of Unknown."

Pesticides in Bottom Sediments, Gas Chromatography with Electron Capture

4. References

- 4.1 Burchfield, H.P. and Johnson, D.E., 1965. Manual of Methods for the Analysis of Pesticide Residues. Southwest Research Institute (Prepared for DHEW, PHS), Vol. I and II.
- 4.2 Organic Pesticide Subcommittee of Committee on Methods Validation and Analytical Quality Control, FWPCA, 1968. Provisional Interim Official Methods for Chlorinated Hydrocarbon Pesticides in Water and Wastewater by Gas Chromatography, 1968.
- 4.3 Breidenbach, A.W., et. al. 1966. The Identification and Measurement of Chlorinated Hydrocarbon Pesticides in Surface Waters. U.S. Department of Health, Education, and Welfare, Public Health Service WP-22 November.
- 4.4 Burke, J. and Giuffrida, A.L. 1964. Investigation of Electron Capture Gas Chromatography for the Analysis of Multiple Chlorinated Pesticide Residues in Vegetables. J. Assoc. Off. Agr. Chemists 47:326.
- 4.5 Hundley, J. C. et. al., 1964. Pesticide Analytical Manual (Vol. II). U. S. Department of Health, Education, and Welfare, Food and Drug Administration.
- 4.6 Shuman, H. and Collie, J.R., 1963. Gas Chromatographic Columns for Optimum Recovery of Chlorinated Pesticides. J. Assoc. Off. Agr. Chemists. 46: 992.
- 4.7 U.S. Dept. of the Interior, FWPCA, 1968. Report on Insecticides in Lake Michigan prepared by Pesticide Committee of the Lake Michigan Enforcement Conference, Donald I. Mount, Ph. D., Chairman, National Water Quality Laboratory, Duluth, Minn.

PESTICIDES IN BOTTOM SEDIMENTS

Microcoulometric Gas Chromatograph

1. General Discussion

Principle: The microcoulometric titration cell used as a gas chromatographic detector has for its basis the coulometric titration of resultant ions with electrically generated ions. Inorganic ions are produced when the effluent from the gas chromatographic column enters the combustion furnace where any organic pesticide hydrocarbons present are broken down into inorganic species.

2. Apparatus

2.1 Dohrmann Model C-200 microcoulometer equipped with microcoulometric titration cells.

2.2 Glass, aluminum, or stainless steel 6 ft. column.

3. Reagents

3.1 Solid support Chromosorb W, P, G or Gas Chrom Q, or Anachrom ABS (acid washed dimethyl-dichlorosilane treated. AW-DMCS).

3.2 Stationary phase DC-200, QF-1, OV 17, OV-101, etc.

4. Procedure

4.1 Recommended Operating Conditions*

- a. Furnace temperature 850°C.
- b. Inlet temperature 300°C.
- c. O₂ flow rate 50 cc/min.
- d. N₂ sweep rate 20 cc/min.
- e. Column temperature 190°C or other temperature.
- f. Flow rate (N₂) 100-200 ml/min.
- g. Diameter 1/8 inches (inside diameter).

*Recommended condition may be adjusted depending upon choice of column.

Pesticides in Bottom Sediments, Microcoulometric Gas Chromatograph

4.2 Measurement of Standard Chloride Solution

- a. Set FUNCTION switch to BIAS READ and adjust BIAS MILLIVOLTS with BIAS SET knob to 12 divisions to the left of zero. This supplies 240 bias millivolts to the cell.
- b. Adjust stirring rate in titration cell to about 1/2 full position (NOTE: Be sure the magnet does not decouple.)
- c. Set FUNCTION switch to GENERATOR READ. Generator volt meter should read 0 or to the left of 0. If the meter reads to the right of 0, add fresh electrolyte to the cell and flush through both stopcocks with electrolyte (70% acetic acid) until the meter reads zero or to the left of zero. (NOTE: Final level of electrolyte should be at black mark on cell.)
- d. Turn recorder power and chart on and adjust needle on recorder to zero with RECORDER ZERO knob on coulometer amplifier. (NOTE: Needle on recorder is at 0 when integrator draws a straight line.)
- e. Set FUNCTION switch to OPERATE. Set RANGE OHMS to 500 or desired setting and wait until cell generates as much titrant as it needs to reach null.
- f. Using a 10 μ l syringe, inject a few micrograms of standard chloride solution directly into the titration cell through the filling funnel. (NOTE: Tip of needle must be below the level of the electrolyte before injection.)

4.3 Measurement of Area Under Peak

- a. Each traverse of the integrator pen represents 10 disc integrator units (DU). Find the total number of DU under the peak.
- b. $1 \text{ DU} = \frac{1}{130} \text{ square inch}$
Calculate the area in square inches under the peak.

Pesticides in Bottom Sediments, Microcoulometric Gas Chromatograph

- c. Calculate the micrograms of chloride represented by this area using the following formula:

$$\mu\text{g chloride} = \frac{\text{Peak area (in sq. in.)} \times 442}{\text{Range OHMS} \times 100}$$

- d. Calculate the recovery of chloride ion in the titration cell using the following formula:

$$\% \text{ Recovery Titration Cell} = \frac{\mu\text{g chloride recovered (as measured area under peak)}}{\mu\text{g chloride injected}}$$

If % recovery is below 90%, clean electrodes in NH_4OH and rinse thoroughly with distilled water before returning to titration cell. Check % recovery again before injection samples into the gas chromatograph.

4.4 Measurement of Standard Pesticide Solution

- With RANGE-OHMS at 000 and the vent closed, zero the recorder. Increase RANGE-OHMS to 050 or other desired range-OHMS and wait until cell reaches null.
- With VENT open inject 200 μg of aldrin into the gas chromatograph. Depress MARK button.
- After one minute, close vent and wait for aldrin peak.
- Using the disc integrator, calculate the area under the peak.
- Calculate the micrograms of aldrin represented by this area using the following formula: (or by calculation given under injection of unknown)

$$\mu\text{g compound} = \frac{\text{Peak Area (in sq. in.)} \times 442}{\text{Range OHMS} \times (\% \text{ chlcrine in compound})}$$

(Reference 7.6 gives the percentage chloride composition of some common chlorinated hydrocarbons.)

- Calculate the recovery of pesticide in the gas chromatographic system using the following formula:

$$\% \text{ recovery total} = \frac{\mu\text{g of pesticide recovered (as measured by area under peak)}}{\mu\text{g of pesticide injected}}$$
- Measure peak area using triangulation and the half-width methods and compare the results with integration.

Pesticides in Bottom Sediments, Microcoulometric Gas Chromatograph

4.5 Measurement of Unknown

- a. With RANGE-OHMS at 000 and vent closed, zero the recorder. Set RANGE-OHMS to desired ohms and wait until cell reaches null.
- b. With VENT open, inject appropriate amount of unknown. Depress MARK button.
- c. After one minute, close the vent and wait for unknown peak(s).

5. Calculations

$$\frac{\mu\text{g}}{\text{kg}} = \frac{\text{ngSTD} \left(\frac{A \text{ unk}}{A \text{ STD}} \right) \text{F. V.} \times 10^3}{\mu\text{l inj.} \times \text{g sample}}$$

μg = Microgram

ng = Nanogram

$A \text{ unk}$ = Area Peak of Unknown

$A \text{ STD}$ = Area Peak of Standard

$\mu\text{l inj.}$ = Microliters extract injected

g sample = Grams of Sample

F. V. = Final volume in milliliters

6. Recovery

- 6.1 Weigh 100 g of bottom sediment sample into a biologically clean sampling bottle.
- 6.2 To 50 ml hexane in a small beaker, add a known amount of pesticide standard (in the concentration range of interest).
- 6.3 Carefully add the pesticide standard solution (with stirring) onto the sample.
- 6.4 Allow the solvent to evaporate at room temperature (stir periodically; this may take a day or two).
- 6.5 When solvent has completely evaporated, transfer sample to Soxhlet extractor and carry out procedure for analysis as in Section 4.2.
- 6.6 Calculate the recovery using the following formula:

$$\% \text{ recovery} = \frac{\text{amount of pesticide found by MCGC}}{\text{known amount of pesticide added}}$$

Pesticides in Bottom Sediments, Microcoulometric Gas Chromatograph

7. References

- 7.1 Barry, H. C. et. al., 1965. Pesticide Analytical Manual (Vol. I revised). U.S. Department of Health, Education, and Welfare, Food and Drug Administration.
- 7.2 Breidenbach, A. W. et al., 1966. The Identification and Measurement of Chlorinated Hydrocarbon Pesticides in Surface Waters. U.S. Department of Health, Education, and Welfare, Public Health Service WP-22 November.
- 7.3 Hundley, J. C. et. al., 1964. Pesticide Analytical Manual (Vol. II). U. S. Department of Health, Education, and Welfare, Food and Drug Administration.
- 7.4 Burchfield, H. P. and Johnson, D.E., 1965. Manual of Methods for the Analysis of Pesticide Residues. Southwest Research Institute (Prepared for DHEW, PHS), Vol. I and II.
- 7.5 Burke, J. and Giuffrida, A. L., 1964. Investigation of Electron Capture Gas Chromatography for the Analysis of Multiple Chlorinated Pesticide Residues in Vegetables. J. Assoc. Off. Agr. Chemists 47:326.
- 7.6 Dohrmann Instruments Company, 1966. Preliminary Operation Instruction for Dohrmann Microcoulometric Titrating System.

PESTICIDES IN BOTTOM SEDIMENTS

Thin Layer Chromatography

1. General Discussion

Thin layer chromatography (TLC) is one of the most widely used analytical and clean up techniques employed in chromatography. Separation of compounds having various polarities, water solubilities and having different carbon chain lengths can be separated by TLC.

1.1 Principle:

- a. Separation and purification of a chemical mixture is effected in thin layer chromatography by forced movement of a spot of material with the aid of a suitable migrating solvent through a thin layer of sorbent material which has been applied to an appropriate support. The mechanism of separation is one or more of the following: adsorption, partitioning or reversed phase partitioning.
- b. Adsorption is useful for the separation of lipophilic organic compounds of low or medium polarity. The adsorption material used is silica gel or aluminum oxide.
- c. Partitioning is useful for the separation of water soluble, inorganic compounds or quite polar organic materials. (Paper was formerly used, but now, cellulose crystalline powder or ground fibers is being used; although unactivated silica gel, carrying an absorbed phase of water can be used.)
- d. Reversed phase partition TLC is good for resolving closely related lipophilic materials like an homologous series differing only in carbon chain length.

2. Apparatus

- 2.1 Plates, 200 mm x 200 mm (8" x 8") glass.
- 2.2 Chamber, glass developing, with lid, 8½" x 4" x 8½".
- 2.3 Spreader, variable thickness.
- 2.4 Spotting template.
- 2.5 Chromatography sprayer.

Pesticides in Bottom Sediments, Thin Layer Chromatography

- 2.6 Desiccator to accommodate 200-mm plates.
- 2.7 UV light box.
- 2.8 Micropipets, 1 μ l-5 μ l-10 μ l, 100 μ l.
- 2.9 Eye droppers.
- 2.10 Spatulas.
- 2.11 Graduated centrifuge test tubes, capacity 15 ml.
- 2.12 Glass wool, pre-extracted with chloroform.
- 2.13 Centrifuge.
- 2.14 Cylinder, 100 ml.
- 2.15 Drying rack to hold 8" x 8" glass plates.
- 2.16 Volumetric flask, 10 ml.

3. Reagents

- 3.1 Pesticide standards.
- 3.2 Rhodamine B base, spirit soluble 0.10 mg/ml in ethanol.
- 3.3 Aluminum Oxide G.
- 3.4 All solvents are redistilled before use.
- 3.5 Hexane: ethyl ether; 4:10 mixture.
- 3.6 Carbon Tetrachloride.
- 3.7 Hexane.

4. Procedure

4.1 Preparation of Plates

- a. Weigh a 40 gram aliquot of Al_2O_3 in a 500 ml centrifuge bottle and add 80 ml 0.03 N HNO_3 . Shake well and centrifuge at 1200 rpm for 1-2 minutes.

Pesticides in Bottom Sediments, Thin Layer Chromatography

- b. Decant the supernatant liquid into a 100 ml graduated cylinder, and record the volume (35-40 ml should be recovered).
- c. Add 80 ml distilled H_2O , break up cake on the bottom of the bottle with a glass rod, shake well and centrifuge as before, and decant and record the volume of the supernatant liquid recovered (70-80 ml).
- d. Repeat the washing step with two additional 80 ml portions of H_2O . Centrifuge and decant as before.
- e. Weigh the Al_2O_3 and H_2O which has been retained (approximately 100 g).
- f. Add 10 ml 1.0% $AgNO_3$ and enough H_2O to make the total weight 120 g, and shake well, place in applicator and prepare plates.
- g. Let plates dry on mounting board for approximately 15 minutes.
- h. Place in a drying rack in a vertical position at $100^\circ C$ for 30 minutes.
- i. Remove the plates and store in a desiccator.

4.2 Spotting Plates

- a. Position plate on Kimwipe or clean surface and scrape $1/4"$ area on two sides of plate.
- b. Insert (5 μ l) capillary spotting tube in small beaker of hexane and touch to folded Kimwipe until all hexane has been removed from capillary. Repeat this five times.
- c. Place template with graduated edge over the aluminum oxide $AgNO_3$ impregnated plate about 1" from bottom.
- d. Mark this position with pencil on both sides of plate.
- e. Rinse capillary twice with standard pesticide solution removing contents each time on kimwipe.

Pesticides in Bottom Sediments, Thin Layer Chromatography

- f. At graduation 1 of template, touch capillary filled with standard once lightly on plate removing approximately $1/4$ of contents of capillary (plate position #1).
- g. At position #2, spot two times putting $1/2$ the contents of the capillary on the plate. Permit each spot to dry before respotting.
- h. At position #3, spot the contents of the capillary (5 μ l) standard by lightly touching the capillary to the plate, removing about $1/4$ of the contents with each spotting. Permit the spots to dry before respotting.
- i. At positions #4 - #6 spot sample labelled "unknown," repeat spotting procedure as described in items f - h. Repeat above procedure for other pesticide solutions and standards.

4.3 Spot Development

- a. Place plate, coated surface facing solvent saturated paper, in developing tank containing 1 cm depth of carbon tetrachloride with marked spotting line down; develop to the 10 cm line.
- b. Lift off top of jar, mark solvent front on side of plate and remove plate, lifting plate with finger tips of both hands. Dry in air for 10 minutes.
- c. Place in an ultraviolet light box and expose for 15 minutes.
- d. Measure the distance of centers of the spots from starting line and compute the R_f values. Record data on data sheet.

4.4 Identification and Estimation Using Rhodamine B

- a. Repeat spotting procedure described above employing aluminum oxide plain plates. Spot the standards and bottom sediments extract sample and develop in solvent tank.
- b. Place plate in hood and spray with Rhodamine B 0.1 g/l in ethanol. The spray should be a fine mist giving an even, smooth light pink color to surface of plate.

Pesticides in Bottom Sediments, Thin Layer Chromatography

- c. Place plate in dark and observe spots with UV light.
- d. Measure distance (cm) of spotting line to solvent front.
Measure distance of spots from starting line.

5. Calculations

- 5.1 Calculate R_f of spots which appear in samples.

$$R_f = \frac{\text{Distance of spot from starting line}}{\text{Distance of solvent front from starting line}}$$

- 5.2 Identify unknowns by comparing R_f value with standards.
- 5.3 Estimation of concentration in unknown spots may be done by comparing with standard pesticide spots.

6. Preparation of Thin Layer Spots for Gas Chromatography

6.1 Marking off Spot Area on Plate

- a. Place template below lower spot line. Mark surface with spatula across plate.
- b. Move template above these spots and similarly mark surface.
- c. Move template to a line above the pesticide spots and mark surface.
- d. Select the lowest concentration of pesticide spots showing best color development, such as, 1.25, 2.50, 5.0 or 10 μ l spots.
- e. Turn template perpendicular to selected spot; mark surface across plate.
- f. Move template to other side of spot and mark surface.

6.2 Removal of Spot from Plate

- a. Insert a tuft of glass wool and position at the tapered end of medicine dropper.
- b. Mark the medicine dropper to identify the pesticide spot collected.

Pesticides in Bottom Sediments, Thin Layer Chromatography

- c. Connect vacuum tubing over tapered end of medicine dropper.
- d. Collect all of adsorbent surface enclosed between boundaries of marked off area by sucking the adsorbent and pesticide by vacuum and depositing in glass wool of medicine dropper.

6.3 Elution of Pesticide

- a. Mark a 10 ml volumetric flask according to the pesticides studied.
- b. Place paper clip over tapered end of medicine dropper approximately $\frac{2}{3}$ distance from large end.
- c. Insert tapered end of dropper into volumetric flask supported by paper clip.
- d. Elute pesticide with 5 ml of 4:1 hexane-ether mixture.
- e. Fill to mark with hexane.
- f. The elute is now ready for further identification by gas chromatography.

7. Reference

Barry, H. C., et. al. 1965 Pesticide Analytical Manual (Revised Vol.I).
U.S. Department of Health, Education, and Welfare, Food and Drug
Administration.

PESTICIDES IN BOTTOM SEDIMENTS

Infrared

1. General Discussion

This method is suitable for mg amounts; but with beam condenser or internal reflectance accessories, μ g quantities may be analyzed.

2. Apparatus

2.1 Twelve ton press with a KBr pellet maker.

2.2 Agate mortar and pestle - approximately 40-75 mm OD.

2.3 I. R. spectrophotometer with beam condenser, internal reflectance, and scale expansion.

3. Reagents

Potassium bromide, infrared quality.

4. Procedure

4.1 Grind 50-100 mg of KBr (dried overnight at 150°C) and mix 50 ng of sample or standard. (This may be done under IR lamp.)

4.2 Press into KBr-disc. (Disc should be clear.)

4.3 Dry 2 hours in a vacuum oven at 50°C and 1 mm/Hg.

4.4 Place disc in spectrophotometer and record IR spectrum.

4.5 Run standards in the same manner.

5. Calculations

Compare IR fingerprints with standards for positive identification.

6. References

6.1 Breidenbach, A.W., et.al. 1966. The Identification and Measurement of Chlorinated Hydrocarbon Pesticides in Surface Waters. U.S.Dept. of Health, Education, and Welfare, Public Health Service WP-22 November.

6.2 Burchfield, H.P. and Johnson, D.E., 1965. Manual of Methods for the Analysis of Pesticide Residues. Southwest Research Institute (Prepared for DHEW, PHS), Vol. I and II.

Pesticides in Bottom Sediments, Infrared

- 6.3 Perkin-Elmer Corp., 1967. How to Collect Fractions from the Model 800 Series Gas Chromatograph. GC Newsletter, Vol. 3, No. 1, Norwalk, Connecticut.
- 6.4 Sadtler, T. and P. Sadtler, 1965. Improved KBr Techniques presented: Pittsburg Conference on Analytical Chemistry and Applied Spectroscopy, Sadtler Research Labs., Inc., 3314 Spring Garden Street, Philadelphia, Pa.

1. General Discussion

- 1.1 Principle: Phenolic types of compounds but not paracresol and similar parasubstituted phenol's react with amino antipyrine at a pH 10.0 ± 0.2 in the presence of ferricyanide to form an antipyrine dye. The dye is extracted with chloroform from the aqueous solution and the absorbance read at 460 m μ .
- 1.2 Interference: Most interferences are eliminated or reduced to a minimum by using the distillate of the original sample.
- 1.3 Minimum Detectable Concentration: The minimum detectable quantity is 0.5 microgram with a 25 ml extraction and when a 5 cm cell is used in the photometric measurement.

2. Apparatus

- 2.1 Distillation apparatus, all glass. A suitable assembly consists of a 1 liter pyrex distilling apparatus with Graham condenser.
- 2.2 Separatory funnels, Squibb form with teflon stoppers 1,000 ml capacity.
- 2.3 Spectrophotometer.

3. Reagents

- 3.1 Phenol Stock Solution: Dissolve 1.0000 g of phenol in distilled water and dilute to 1,000 ml with distilled water. 1 ml = 1 mg phenol
- 3.2 Phenol Working Solution: (Must be prepared daily) Pipette 20.0 ml of stock solution into a 1 liter volumetric flask and dilute to volume with distilled water. 1 ml = 0.020 mg
- 3.3 Phenol Standard Solution: Pipette 25.0 ml of working solution into a 500 volumetric flask and dilute to volume with distilled water. 1 ml = 0.001 mg
- 3.4 Ammonium Chloride Solution: Dissolve 67.5 g of NH_4Cl in 570 ml of conc. NH_4OH and dilute to one liter with distilled water.
- 3.5 Aminoantipyrine Solution: Dissolve 2.0 g of 4 - aminoantipyrine in distilled water and dilute to 100 ml volume.
- 3.6 Potassium Ferricyanide Solution: Dissolve 8.0 g $\text{K}_3\text{Fe}(\text{CN})_6$ in distilled water and dilute to 100 ml.

Phenol in Bottom Sediments

- 3.7 Chloroform: Reagent grade of chloroform (redistilled).
- 3.8 Phosphoric Acid Solution: Mix 10 ml of phosphoric acid with distilled water and dilute to 100 ml.
- 3.9 Copper Sulfate Solution: Dissolve 10 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water and dilute to 100 ml.

4. Procedure

- 4.1 An aliquot of sample containing not more than 50 μg of phenol is placed in the distilling flask. (20 g)
- 4.2 Add 550 ml of distilled water.
- 4.3 If the sample has not been preserved, add 5 ml of 10% CuSO_4 and phosphoric acid and a few drops of methyl orange indicator.
- 4.4 Add a few boiling chips and distill over 500 ml of distillate.
 - 4.4a If oil is present in distillate, filter through two thicknesses of dry No.12 Whatman filter paper into separatory funnel to remove oil.
- 4.5 Transfer the distillate to a one liter separatory funnel, add 3 ml of NH_4Cl and mix, 3 ml of aminoantipyrine and mix, and 3 ml of potassium ferricyanide and mix. Let stand at least 3 minutes.
- 4.6 Add 25 ml of CHCl_3 and shake vigorously for 30 seconds: after the layers have separated, shake once more for 30 seconds.
- 4.7 When the layers have separated, draw the CHCl_3 layer off through a cotton pledget placed in the stem of the separatory funnel into a 25 ml graduate cylinder. (Do not make to volume.)
- 4.8 Read the optical density at a wave length of 460 $\text{m}\mu$.
- 4.9 Standards and blanks are treated exactly as the sample.

5. Calculations

5.1 Wet basis

$$\text{mg/kg} = \frac{\text{mg in Std.}}{\text{O.D. Std.}} \times \frac{\text{O.D. Sample}}{\text{grams Sample}} \times 1000$$

5.2 Dry basis

$$\text{mg/kg} = \frac{\text{mg/kg wet basis}}{\% \text{ Solids (decimal fraction)}}$$

6. Reference

Standard Methods for the Examination of Water and Wastewater, 12th Ed., APHA, Inc., N.Y., 1965, 514-520.

TOTAL SOLUBLE PHOSPHORUS IN BOTTOM SEDIMENTS

1. General Discussion

- 1.1 Principle: Ammonium molybdate and potassium antimonyl tartrate react in an acid medium with dilute solutions of orthophosphate to form a heteropoly acid (phosphomolybdic acid) which is reduced to the intensely colored molybdenum blue by ascorbic acid.
- 1.2 Interferences: Arsenates react with the molybdate reagent to produce a blue color similar to that formed with phosphate. Concentrations as low as 0.10 mg/l of arsenic interfere with the phosphate determination. Hexavalent chromium and nitrite interfere to give results about 3% low at concentrations of 1.0 mg/l and 10-15% low at concentrations of 10 mg/l chromium and nitrite. Sulfide (Na_2S) and silicate do not interfere in concentrations of 1.0 and 10 mg/l.
- 1.3 Precautions: All glassware should be washed with hot 1:1 hydrochloric acid and then rinsed thoroughly with distilled water. The glassware is then filled with distilled water and all reagents added and allowed to stand 15 or 20 minutes, followed by a distilled water rinse. Commercial detergents should not be used.

2. Apparatus

Colorimetric equipment: A spectrophotometer with an infrared phototube for use at 880 $\text{m}\mu$, providing a light path of 1" or longer, should be used.

3. Reagents

- 3.1 1.0 N H_2SO_4 .
- 3.2 1.0 N NaOH.
- 3.3 1.0 N NaOH.
- 3.4 Sulfuric Acid, 8N: Dilute 112 ml of conc. H_2SO_4 with distilled water to 500 ml.
- 3.5 Potassium Antimonyl Tartrate: Dissolve 4.3888 g $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 1/2 \text{H}_2\text{O}$ in 200 ml of distilled water. Store in dark bottle at 4°C.

Total Soluble Phosphorus in Bottom Sediments

- 3.6 Ammonium Molybdate Solution: Dissolve 20 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 500 ml of distilled water. Store in plastic bottle at 4°C .
- 3.7 Ascorbic Acid, 0.1M: Dissolve 1.76 g of ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if stored at 4°C .
- 3.8 Combined Reagent: Mix the above reagents in the following order and proportions for 100 ml of the combined reagent: to 50 ml of 8N H_2SO_4 , add 5 ml of potassium antimonyl tartrate solution and mix, then add 15 ml of ammonium molybdate solution and mix, and finally, 30 ml of ascorbic acid solution and mix. All reagents must be at room temperature before mixing. The combined reagent should be prepared fresh each day just before use.
- 3.9 Alcohol, ethyl (95 per cent) or isopropyl.
- 3.10 Stock Phosphorus Solution: Dissolve in distilled water 2.1968 g of potassium dihydrogen phosphate, KH_2PO_4 , which has been dried in an oven at 105°C . Dilute this solution to 1,000 ml. One ml equals 0.50 mg P.
- 3.11 Working Phosphorus Standard #1: Dilute 20 ml of stock phosphorus solution to 1,000 ml with distilled water, 1 ml equals 0.01 mg P.
- 3.12 Dilute 100 ml of working standard #1 to 1,000 ml with distilled water, 1 ml equals 0.001 mg P.
- 3.13 Strong Acid Solution: Slowly add 300 ml conc. H_2SO_4 to 600 ml distilled water. When cool, add 4.0 ml conc. HNO_3 and dilute to 1 liter.
- 3.14 Potassium or ammonium Persulfate, analytical grade.
- 3.15 Concentrated HNO_3 .

4.

Procedure

- 4.1 Place 5 g of well blended sample into a 100 ml beaker. Add 50 ml of distilled water and mix. Let this solution set overnight at room temperature.
- 4.2 Filter the above mixture through a membrane filter 0.45 μ porosity and place entire filtrate in a 250 ml beaker. Do no wash residue on filter.
- 4.3 Add 1 ml of strong acid and 0.4 g of potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$). Boil gently for 90 minutes, adding distilled water if necessary to keep the volume between 25 and 50 ml.

Total Soluble Phosphorus in Bottom Sediments

- 4.4 Cool, neutralize to a faint pink color with 1N NaOH and transfer to 100 ml nessler tubes. Dilute to volume.
- 4.5 Add 5 ml of ethyl or isopropyl alcohol and mix thoroughly.
- 4.6 Add 5 ml of combined reagent. Mix thoroughly and allow to stand 10 minutes for color development. Read at 880 mμ.
- 4.7 A standard and blank should also be run with each analysis.

5. Calculations

5.1 Wet Basis

$$\text{mg/kg} = \frac{\text{mg in Std.}}{\text{O.D. Std.}} \times \frac{\text{O.D. Sample}}{(\text{grams sample in aliquot})} \times 1000$$

5.2 Dry Basis

$$\text{mg/kg} = \frac{\text{mg/kg wet basis}}{\% \text{ solids (decimal fraction)}}$$

6. References

- 6.1 "Methods for the Collection and Analysis of Water Samples," Geological Survey Water Supply Paper 1454, 1960, pp 245-250.
- 6.2 Official Methods of Analysis, A.O.A.C., 7th Ed., 1950, p 370.
- 6.3 Journal AWWA, July 1965, pp 917-925.

TOTAL PHOSPHORUS IN BOTTOM SEDIMENTS

1. General Discussion

- 1.1 Principle: Ammonium molybdate and hydrazine sulfate react in an acid medium with dilute solutions of orthophosphate to form a heteropoly acid (phosphomolybdic acid) which is reduced to the intensely colored molybdenum blue by sodium sulfite.
- 1.2 Interferences: Arsenic, iron, tungsten, silica, titanium, zirconium and vanadium do not interfere.
- 1.3 Precautions: All glassware should be washed with hot 1:1 hydrochloric acid and then rinsed thoroughly with distilled water. The glassware is then filled with distilled water and all reagents added and allowed to stand 15 to 20 minutes, followed by a distilled water rinse. Commercial detergents should not be used.

2. Apparatus

Colorimetric equipment: A spectrophotometer with an infrared phototube for use at 810 μ , providing a light path of 1" or longer should be used.

3. Reagents

- 3.1 3% H_2O_2 .
- 3.2 Perchloric acid.
- 3.3 50% $Mg(NO_3)_2 \cdot 6H_2O$: Dissolve 500 g $Mg(NO_3)_2 \cdot 6H_2O$ in 1,000 ml of distilled water.
- 3.4 Concentrated hydrochloric acid.
- 3.5 10% Na_2SO_3 : Dissolve 100 g Na_2SO_3 (phosphate free) in 1,000 ml of distilled water. Prepare fresh daily.
- 3.6 0.15% Hydrazine Sulfate: Dissolve 1.5 g of the salt in 1,000 ml of distilled water. Prepare fresh daily.
- 3.7 Ammonium Molybdate: Add 300 ml of conc. H_2SO_4 to 500 ml of distilled water and cool to room temperature. Dissolve 20g of ammonium molybdate in the H_2SO_4 solution and dilute to 1,000 ml with distilled water. (Do not use the regular 1:1 - H_2SO_4 for this - mix as directed.)

Total Phosphorus in Bottom Sediments

- 3.8 Mixed Reagent: Dilute 25 ml of ammonium molybdate solution with 45 ml of distilled water. Add 10 ml of the hydrazine sulfate solution and 20 ml of the sodium sulfite solution, and dilute to 100 ml with distilled water. The reagent is stable for about one-half hour.

4. Procedure

- 4.1 Weigh 1.00 g of well-blended sample into a 250 ml Vycor dish.
- 4.2 Add 10 ml of 3% H_2O_2 and heat on hot plate for 10 or 15 minutes with stirring to prevent overflowing from frothing.
- 4.3 Add 10-15 ml of distilled water and continue to boil until frothing has ceased and almost all of the water has evaporated.
- 4.4 Add 10 ml of 50% $Mg(NO_3)_2 \cdot 6H_2O$ and place in a cold muffle furnace. (Keep stirring rod in Vycor dishes and make sure dishes are permanently marked.)
- 4.5 Start at 100°C and increase the heat gradually until the samples are dry (about 350°C). Then increase heat to 500-550°C and ash for one hour.
- 4.6 Remove samples from furnace and let cool on asbestos pads.
- 4.7 When cool, add 20 ml of conc. HCl, place on hot plate and heat with stirring until effervescence has stopped.
- 4.8 Add approximately 50 ml of distilled water and clean the sides of the dish with a rubber policeman.
- 4.9 Filter through membrane filter 0.45 μ into a 250 ml volumetric flask, wash dish and filter paper with distilled water and make up to volume.
- 4.10 Take a 25 ml aliquot, add 4 ml perchloric acid and fume until fumes reach the mouth of the flask.
- 4.11 Cool, then add 10 ml of distilled water, 15 ml of 10% Na_2SO_3 and boil for at least one minute, but not longer than two minutes.
- 4.12 Cool, then add 20 ml of the mixed reagent and heat in a boiling water bath for 15 minutes and cool rapidly to 20°C.
- 4.13 Transfer to a 100 ml nessler tube and make up to volume with distilled water and read at 810 m μ against distilled water. The usual blank for reagents is 0.015.

Total Phosphorus in Bottom Sediments

5. Calculations

5.1 Wet Basis

$$\text{mg/kg} = \frac{\text{mg in Std.}}{\text{O.D. Std.}} \times \frac{\text{O.D. Sample}}{\text{(grams sample in aliquot)}} \times 1,000$$

5.2 Dry Basis

$$\text{mg/kg} = \frac{\text{mg/kg wet basis}}{\% \text{ solids (decimal fraction)}}$$

6. References

- 6.1 "Methods for the Collection and Analysis of Water Samples," Geological Survey Water Supply Paper 1454, 1960, pp 245-250.
- 6.2 Official Methods of Analysis, A.O.A.C., 7th Ed., 1950, p 370.
- 6.3 Journal AWWA, July 1965, pp 917-925.
- 6.4 Chemical Analysis of Iron and Steel, Lindell, Hoffman and Bright, 1931, pp 209-231.
- 6.5 U.S. Bureau of Mines, Minneapolis, Minnesota, Personal Communication.

SOLIDS - TOTAL AND VOLATILE IN BOTTOM SEDIMENTS

1. General Discussion

- 1.1 Principle: The sample is dried in a weighed dish in an oven at 103-105°C to constant weight. The increase in weight over that of the empty dish represents the total solids.
- 1.2 The volatile solids are determined by placing the oven dried sample from 1.1 in the muffle furnace for one hour at 600°C. The decrease in weight of residue after ashing represents the volatile solids.
- 1.3 Minimum detectable concentration: Dependent on the sensitivity of the analytical balance used for weighing.

2. Apparatus

- 2.1 Drying Oven.
- 2.2 Muffle Furnace.
- 2.3 Porcelain Crucibles.
- 2.4 Porcelain Evaporating Dishes.
- 2.5 Analytical Balance.

3. Procedure

- 3.1 Wash dishes and number with heat-resistant marking pencil.
- 3.2 Place evaporating dishes in a muffle furnace at a temperature of 600-650°C for one hour.
- 3.3 Remove evaporating dishes from the furnace and allow them to cool for 1-2 minutes in air, but not more than 3-4 minutes. Then place them in a dessicator for 1 hour.
- 3.4 Weigh and record this weight as the tare weight.
- 3.5 Weigh 10 grams of bottom sediment to the nearest 0.01 grams in the tared evaporating dishes.
- 3.6 Place the sample in the oven at 103-105°C overnight.
- 3.7 Remove samples from the oven and place them in a dessicator for 1 hour.
- 3.8 Weigh and record this weight as the oven-dry weight.
- 3.9 Place the oven dried sample in the muffle furnace at 600°C for 1 hour.

Solids - Total and Volatile in Bottom Sediments

3.10 Remove samples from the furnace and allow them to cool for 1-2 minutes in air, but not more than 3-4 minutes. Afterwards, place them in a dessicator for 1 hour.

3.11 Weigh and record this weight as the furnace weight.

4. Calculation

4.1 $\frac{\text{Oven dry weight}}{\text{Initial wt. of sample}} \times 100 = \% \text{ total solids}$

4.2 $\frac{\text{Oven dry weight} - \text{furnace weight}}{\text{Oven dry weight}} \times 100 = \% \text{ volatile solids}$

5. Reference

Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965, 534-535.

TOTAL SULFIDE IN BOTTOM SEDIMENTS

1. General Discussion

Total sulfide includes dissolved hydrogen sulfide and its ionization products as well as acid-soluble metallic sulfides present in suspended matter. Sulfide ion is also determined by the following method, but it is not present in significant concentrations below a pH of 13.

- 1.1 Principle: Sulfides are removed from suspended matter and other interfering substances in solution by distillation under acidic conditions. Air oxidation of the evolved hydrogen sulfide is minimized by passing nitrogen gas through the system which displaces the oxygen prior to acid addition. The distilled hydrogen sulfide is collected in zinc acetate which reacts to form insoluble zinc sulfide.

The zinc sulfide is reacted with N,N-Dimethyl-p-phenylenediamine and sulfuric acid to produce an intermediate that is oxidized by ferric chloride to an intensely blue colored dye called methylene blue. The intensity of the blue color is proportional to the original concentration of sulfide in the distillate and is measured at a wave length of 650 mμ.

- 1.2 Sampling and storage: Samples must be taken with a minimum of aeration, for not only are sulfides volatilized by aeration but also any oxygen that is taken up will readily oxidize the sulfides to free sulfur.

The sample is preserved by pipetting 2 ml of 2N zinc acetate solution into the bottle, replacing the stopper, and shaking well. This precipitates the sulfides as inert zinc sulfide, which not only prevents oxidation of sulfides but also prevents further sulfide generation.

2. Apparatus

- 2.1 Distillation apparatus, all glass. For large samples, a suitable assembly consists of a 1-liter pyrex distilling flask with Graham condenser as used for the analysis of phenols.

A section of glass tubing should be connected to the tip of the condenser so that it reaches the bottom of the collection tube.

- 2.2 Distillate collection tubes. Short form Nessler tubes. graduated at 50 and 100 ml.
- 2.3 Spectrophotometer, for use at 650 mμ and providing a light path of 1 inch or greater.

3. Reagents

- 3.1 Nitrogen, water-pumped.
- 3.2 Zinc acetate, 2N. Dissolve 220 g of Zn (C₂H₃O₂)₂·2H₂O in distilled water and dilute to 1 liter.
- 3.3 Zinc acetate, 0.2N. Add several drops of acetic acid to 100 ml of 2N zinc acetate solution and dilute to 1 liter.
- 3.4 Sulfuric acid solution, 1:1. Add, cautiously, 500 ml of conc. H₂SO₄ to 500 ml of distilled water in a 1-liter flask. Mix continuously and cool under running water while combining reagents. Cool solution before using.
- 3.5 Dilute sulfuric acid solution, approx. 0.1N: Dilute 5 ml of 1:1 H₂SO₄ to 1 liter with distilled water.
- 3.6 Stock amine solution: Dissolve 2.7 g of N,N-Dimethyl-p-phenylenediamine sulfate and dilute to 100 ml with 1:1 H₂SO₄ solution. This solution is stable for approximately one week.
- 3.7 Working amine solution. Dilute 2 ml of stock amine solution to 100 ml with 1:1 H₂SO₄ solution. Prepare fresh daily.
- 3.8 Ferric chloride solution: Dissolve 100 g of FeCl₃·6H₂O in hot distilled water and dilute to 100 ml. Cool before use.
- 3.9 Standard potassium biniodate solution, 0.025N. Accurately weigh out 0.8124 g KH(IO₃)₂ and dissolve in distilled water. Dilute to 1-liter.
- 3.10 Standard sodium thiosulfate titrant, 0.025N. Dissolve 6.205 g N₂S₂O₃·5H₂O in distilled water and dilute to 1 liter. Preserve with 5 ml chloroform. Standardize against standard potassium biniodate using starch as an indicator.

- 3.11 Potassium iodide solution. Dissolve 5 g of KI in distilled water and dilute to 100 ml.
- 3.12 Treated hydrochloric acid. Place one or two strips of aluminum in a small beaker of concentrated HCl. After violent reaction, the acid is poured off and is ready to use.
- 3.13 Oxygen-free dilution water. Pass nitrogen gas through a sufficient quantity of distilled water for dilution requirements. A minimum of 10 minutes is required to displace oxygen in the water.
- 3.14 Sodium sulfide, Reagent, crystal.

4. Procedure

- 4.1 Standardization: Sulfide solutions are extremely unstable and must be prepared fresh and used immediately. Stability is increased by using nitrogen-saturated water for dilution, etc.

Prepare 0.01N sulfide solution as follows: Weight out approximately 1.2 g of large crystal $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. Wash the crystals several times with distilled water. Discard the washings and add the washed crystals to 975 ml of nitrogen-saturated distilled water. Dilute to 1 liter. The exact concentration of this stock solution is determined by reacting the sulfide with an excess of iodine to give free sulfur and titrating the unreacted iodine with sodium thiosulfate.

Pipet 20.00 ml of stock sulfide solution into 100 ml of oxygen-free water. Add 5 ml of KI solution, 20.00 ml of 0.025N $\text{KH}(\text{IO}_3)_2$ solution, and 10 ml of 0.1N H_2SO_4 . Titrate with 0.025N $\text{Na}_2\text{S}_2\text{O}_3$ solution using starch as an end point indicator. Carry a blank through the procedure and calculate the amount of reacted iodine from the difference between the blank and standard titrations. Since 1 ml of 0.025N $\text{KH}(\text{IO}_3)_2$ is equivalent to 0.400 mg of sulfide ion, calculate the sulfide concentration in the stock solution. Calculate the ml of stock solution equivalent to 2 mg sulfide and add this amount to 900 ml of oxygen-free water and dilute to 1 liter. This is the working standard containing 2 μg sulfide per ml of solution.

Prepare a standard curve using the working sulfide solution in the range from 2 to 50 μg sulfide, as follows: Pipet 20 ml of 0.2N $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ into a series of 50 ml nessler tubes. Add the required amounts of sulfide solution to each

tube and dilute to 50 ml with oxygen-free water. Develop the color as outlined in section 4.3 and read the optical density at 650 mμ.

Prepare a standard curve for distilled samples by running consecutive amounts of the working standard through the distillation procedure in section 4.2. Determine the sulfide concentration of each standard run through this procedure by adding an identical amount of working standard to 20 ml of zinc acetate, diluting to 50 ml, developing the color and comparing the optical density with the standard curve. This step is necessary since the sulfide concentration in the working standard decreases with time.

- 4.2 Distillation Procedure. Set up the distillation apparatus. The transfer tube from the condenser should reach to the bottom of the distillate collection tube. The condenser should be attached in such a manner that it can be easily moved up or down when diluting the distillate or adding reagents.

Pipet 20 ml of 0.2N $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ into a 100 ml nessler tube and lower the condenser so that the transfer tubing reaches below the level of the liquid. Attach a distilling flask and pass nitrogen gas through the system for at least 10 minutes. Add an aliquot of the bottom sediment sample containing not more than 50 μg of sulfide. Bubble nitrogen gas through the sample to remove any oxygen dissolved in the sample. A small amount of sulfide may be driven over by the gas, so be sure that the only exit is through the zinc acetate solution in the collecting tube. Discontinue nitrogen evolution and add rapidly several boiling stones, 2 drops of methyl orange indicator, and enough treated HCl to change the color from orange to red. Stopper as quickly as possible and heat slowly. The slower the heating rate the greater the contact time between the evolved H_2S and $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ and the less chance of sulfide loss. Distill the solution until approximately 20 ml of distillate have been collected (roughly 5-8 minutes after the solution commences to boil). Turn off heat and remove the stopper in the distillation flask to keep the distillate from being sucked back up the condenser. Raise the transfer tube above the 50 ml mark on the collection container and dilute the solution to 50 mls. Return the transfer tube to the solution and proceed with color development.

4.3 Color Development. Since some zinc sulfide adheres to the transfer tube, it should be in the solution while the color reaction is taking place. Furthermore, since this reaction is sensitive to temperature, the solution should be immersed in a water bath at 23-25°C while reagents are being added. Add 2 ml of dilute amine solution to the 50 ml of distillate, mix and add 5 drops of FeCl_3 solution. Mix again and set aside for 10 minutes while the color develops. Measure the absorbance at 650 m μ .

5. Calculation

5.1 Wet basis:

$$\text{mg/kg} = \frac{\text{mg in Std.}}{\text{O.D. Std.}} = \frac{\text{O.D. Sample}}{(\text{grams Sample in aliquot})} \times 1000$$

5.2 Dry basis:

$$\text{mg/kg} = \frac{\text{mg/kg wet basis}}{\% \text{ Solids (decimal fraction)}}$$

6. References

- 6.1 Photometric Determination of Sulfide and Reducible Sulfur in Alkalies, M. Budd, H. Bewick, Anal. Chem. 24, 1536 (1952).
- 6.2 Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965, 426-432.
- 6.3 A Revised Method for the Determination of Total Sulfide in Water and Bottom Sediments. T. O. Meiggs, Lake Michigan Basin Office, Chicago, Ill. (1966).

SILICA IN BOTTOM SEDIMENTS

1. General Discussion

Although silicon constitutes approximately 26% of the lithosphere, it is never found in the native state. As the silicate, it occurs extensively as a constituent of igneous rocks, quartz and sand. The silica content may serve to differentiate sediment due to erosion from that of industrial and municipal origin.

The classical gravimetric procedure is widely used for determining silica in minerals and other materials e.g., portland cement, glass, etc. which are high in silica content. (7.1, 7.4, 7.5.)

This method includes:

1. Sodium carbonate fusion to decompose refractory silica and other such materials.
2. Double evaporation - dehydration to isolate silica as its insoluble anhydride.
3. Ignition of the residue to constant weight.
4. Volatilization of silica as silicon tetrafluoride.
5. Calculation of the amount of silica from the weight lost or volatilization.

Highly accurate results can be obtained using this method; however, it suffers the following disadvantages: (a) it is quite lengthy and (b) requires the use of expensive platinum equipment. This extreme accuracy is not required when monitoring the silica composition of a large number of sediments.

A modified gravimetric procedure is here proposed for the determination of "uncorrected silica" (7.2) in sediments. Pure or corrected silica can be reported only after the residue has been subjected to the hydrofluoric acid volatilization procedure. "Uncorrected silica" is hereafter referred to as "silica."

2. Apparatus

- 2.1 Porcelain evaporating dishes.
- 2.2 Porcelain crucibles and covers.
- 2.3 Watch glasses, to fit evaporating dishes.
- 2.4 Pestle, large.

Silica in Bottom Sediments

- 2.5 Hot plates, large.
- 2.6 Glass stirring rods.
- 2.7 Filter paper.
- 2.8 Filtering funnels and rack.
- 2.9 Beakers, 400 ml capacity.
- 2.10 Hot water wash bottles.
- 2.11 Drying oven, 110°C.
- 2.12 Fisher burners.
- 2.13 Ring stand and rings.
- 2.14 Clay triangles.

3. Reagents

- 3.1 Hydrochloric acid concentrated.
- 3.2 Hydrochloric acid, 10%.
- 3.3 Nitric acid, concentrated.

4. Procedure

Start with the residue from the determination of volatile solids, contained in a porcelain evaporating dish.

- 4.1 Add 30 ml of concentrated HCl to the residue.
- 4.2 Pulverize with a pestle, taking care not to lose any sample in the process.
- 4.3 Wash the pestle with distilled water using a rubber policeman to dislodge adhering particles.
- 4.4 Add 1 ml of concentrated HNO_3 to each sample.
- 4.5 Place the evaporating dish on a hot plate, cover with a watch glass and evaporate to dryness.
- 4.6 Transfer the evaporating dish from the hot plate to a drying oven and bake at 110°C for 1 hour.

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- 4.7 Set baked residue back on the hot plate, add 15 ml concentrated HCl and heat to dissolve the difficult soluble salts.
- 4.8 Wash any adhering material off the watch glass into the evaporating dish with about 25 ml of distilled water.
- 4.9 Continue heating until all soluble salts are dissolved, filter while hot through an ashless filter paper into a 400 ml beaker (save this filtrate for subsequent analysis).
- 4.10 Wash any residue remaining in the evaporating dish onto the filter paper using a rubber policeman to aid in the removal of adhering particles.
- 4.11 Wash the residue retained on the filter paper free of soluble salts with hot 10% HCl (about 10 times).
- 4.12 Transfer the filter paper containing all the residue to a tared porcelain crucible.
- 4.13 Dry and ignite to constant weight at the hottest temperature attainable with a bunsen burner.
- 4.14 Cool with cover on, weigh and calculate the % SiO₂.

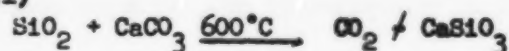
5. Calculations

$$\% \text{SiO}_2 = \frac{\text{g SiO}_2 \times 100}{\text{g dry sample wt.}}$$

6. Discussion of Method

The modified gravimetric method for the determination of silica in sediments utilizes the residue from the determination of volatile solids. It is convenient to use this residue since ignition at 600°C has destroyed interfering organic matter. Furthermore, ignition has served to prepare the sample for analysis, by converting certain insoluble silicates to calcium silicate, which is acid soluble: (7.2)

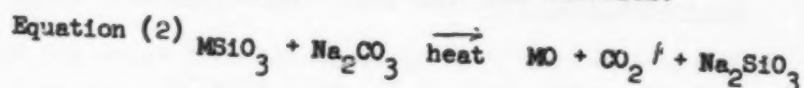
Equation (7.1)



This conversion is highly probable when sediments are ignited since they contain substantial amounts of calcium carbonate.

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The sodium carbonate fusion serves a like function.



Since ignition is noted to serve the same function as fusion, the latter step was excluded from the modified procedure.

The modified procedure also suggests that porcelain ware be used in lieu of platinum. The literature noted that strong hydrochloric and nitric acids, used to decompose the sample, might dissolve some silicates from the porcelain evaporating dish. (7.3) However, it is further noted that, any silicates thus gained hopefully will be negated by adsorption losses when the dehydrated silica is removed from the dish (silica being tenaciously adsorbed by porcelain).

The most time consuming step in the classical gravimetric silica procedure is the one which involves the double evaporation-dehydration of the sample. A reference to the literature indicates that a single evaporation-dehydration step would recover 97-99% of the total silica present in a sample. (7.3)

Investigation has confirmed this recovery rate (See Table 1). A single evaporation-dehydration is used in the modified procedure, since in surveillance work the relative change over a period of time rather than exact amount is most important.

It is expedient to utilize the filtrate from the silica procedure for subsequent determinations of iron and manganese, since interfering organic matter and silica have been removed. (See iron and manganese analysis).

Finally, as noted in the General Discussion (Section 1), silica as determined by the modified procedure is "uncorrected", since the residue was not subjected to a hydrofluoric acid volatilization.

7. References

- 7.1 Snell, F.D., & Biffen, F.M., Commercial Methods of Analysis, New York: McGraw Hill, 1944, pp 176-191
- 7.2 Ayres, G.H., Quantitative Chemical Analysis, New York: Harper Bros., 1958, 245-249.

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- 7.3 Kolthoff, I.M. & Sandell, E.B., Textbook of Quantitative Inorganic Analysis, New York: MacMillan Co., 1946, p.402-403.
- 7.4 Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965 258-260.
- 7.5 "Methods for Collection & Analysis of Water Samples," Geological Survey Water Supply Paper, 1454, 1960, pp 259-263.

TABLE 1
SILICA RECOVERY - SINGLE VS DOUBLE EVAPORATION

Sample No.	A	B	Total Residue A + B	% Silica Recovery By Single Evap.
	Wt. of Residue From Single Evap.-Dehy.	Wt. of Residue From Second Evap.-Dehy		
1	2.9732	0.0032	2.9764	99.89
2	3.2149	0.0022	3.2171	99.93
3	1.3853	0.0040	1.3893	99.71
4	1.3932	0.0015	1.3947	99.89
5	2.5408	0.0015	2.5423	99.94
6	1.0645	0.0008	1.0653	99.92
7	2.4757	0.0003	2.4760	99.98
8	1.9985	0.0040	2.0025	99.80
9	1.4854	0.0016	1.4870	99.89
10	3.5845	0.0110	3.5955	99.69
11	4.6403	0.0104	4.6507	99.77
12	1.0746	0.0017	1.0763	99.84
13	1.1986	0.0037	1.2023	99.69
14	5.1323	0.0089	5.1412	99.82
15	1.6429	0.0063	1.6492	99.61
16	2.1838	0.0008	2.1846	99.96
17	1.3859	0.0034	1.3943	99.39
18	3.7114	0.0007	3.7121	99.98
19	1.5161	0.0021	1.5182	99.86
20	1.0811	0.0004	1.0815	99.96

MANGANESE IN BOTTOM SEDIMENTS

1. General Discussion

- 1.1 Principle: Manganese is readily determined in small concentrations by oxidizing it in acidic solution to the intensely colored permanganate ion and measuring the absorbance of the resulting solution at a wavelength of 525 m μ .

After the sample has been digested with acid to oxidize organic matter and to volatilize chlorides as HCl, phosphoric acid is added to form a colorless complex with ferric ion. Oxidation with persulfate ion is carried out in hot acidic solution in the presence of silver as a catalyst. The color is stable for 24 hours.

- 1.2 Interferences: The most important interferences are organic matter, chloride ion and other reducing substances. These are taken care of in the ashing step. Other colored ions, notably ferric iron, copper, nickel and chromate contribute to the color. The interference of iron is overcome by the addition of phosphoric acid. That of the other ions is compensated for using a portion of the sample from which the permanganate color has been bleached for a blank.
- 1.3 Minimum detectable concentration: If the volume of the sample is 100 ml, the minimum detectable concentration using a 1 inch cell is 0.01 mg/l.

2. Apparatus

Spectrophotometer equipped with absorption cells providing a light path of 1 inch or longer, for use at 525 m μ .

3. Reagents

- 3.1 Stock manganese solution: Dissolve 1.8g potassium permanganate in about 450 ml distilled water in a liter flask and heat 4-5 hours at 70°-80°C protecting the mouth of the flask from dust. Within 24 hours standardize oxidimetrically against sodium oxalate.
- 3.2 Standard manganese solution: The volume of stock solution required to prepare a liter of solution containing 50 mg/l Mn is 4.55 divided by the normality of KMnO_4 . Transfer exactly this volume to a pyrex 1-liter volumetric flask. Add 5 ml conc. H_2SO_4 and then NaHSO_3 dropwise with stirring until the pink color disappears. Boil gently for a few minutes to remove excess SO_2 . Cool and dilute to volume with distilled water.
1 ml = 0.05 mg Mn.

- 3.3 Sulfuric acid, conc.
- 3.4 Special reagent: Dissolve 18.7500 g of mercuric sulfate in 100 ml conc. HNO_3 and 200 ml distilled water. Add 200 ml 85 percent phosphoric acid and 0.85 g silver nitrate and dilute the cooled solution to 1 liter.
- 3.5 Ammonium persulfate, reagent grade.
- 3.6 Sodium bisulfite solution: Dissolve 10g NaHSO_3 in 90 ml distilled water.
- 3.7 Sodium oxalate, primary standard, $\text{Na}_2\text{C}_2\text{O}_4$. (0.2 - 0.4 g anhydrous $\text{Na}_2\text{C}_2\text{O}_4$ weighed to nearest 0.1 mg.)

4. Procedure

- 4.1 Take an aliquot of the filtrate from the determination of silica containing not more than 2.0 mg of Mn.
- 4.2 Transfer this aliquot to a 400 ml beaker, add 5.0 ml concentrated H_2SO_4 . Cover loosely with a watch glass and evaporate on a hot plate to the copious evolution of SO_3 fumes.
- 4.3 Transfer the residue to a 250 ml Erlenmeyer flask, using a minimum amount of water, and again bring to fumes.
- 4.4 Cool, add approximately 75 ml of distilled water and boil to dissolve the soluble salts.
- 4.5 Allow to cool, add 20 ml of the special reagent and 1 g of ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (use a 1 g Hach measuring spoon for this addition).
- 4.6 Quickly heat to boiling and continue to boil for 2 minutes.
- 4.7 Remove the solution from the hot plate, add 0.2 g persulfate (use a 0.2 g Hach measuring spoon) and allow to stand for 1 minute before transferring to an ice bath for further cooling.
- 4.8 Adjust the volume of solution in each flask to 100 ml with distilled water.

Manganese in Bottom Sediments

4.9 Read the absorbance of each solution versus a blank in a spectrophotometer set at a wavelength of 525 mμ.

4.10 Prepare calibration curve covering the range 0-5 mg/l.

5. Calculation

5.1 Wet Basis

$$\text{mg/kg} = \frac{\text{mg Std.}}{\text{OD Std.}} \times \frac{\text{OD Sample}}{\left(\frac{\text{grams Sample}}{\text{in aliquot}} \right)} \times 1000$$

5.2 Dry Basis

$$\text{mg/kg} = \frac{\text{mg/kg wet basis}}{\% \text{ Solids (decimal fraction)}}$$

6. Reference

Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965, 489-492.

OXIDATION-REDUCTION POTENTIAL MEASUREMENTS

The oxidation-reduction (redox or E_h) potential is defined as the electromotive force developed by a platinum electrode immersed in the water or bottom sediment, referred to the standard hydrogen electrode.

This is a measure of the oxygen potential of the bottom sediments. When E_h is positive, this indicates the presence of oxygen or the material is in the oxidized state and when it is negative the absence of oxygen is indicated or the material is in the reduced state. An E_h measurement would give a good indication whether the iron was in the ferric state or the ferrous state.

To measure the potential, a Beckman Zeromatic pH Meter or a Beckman Model N is used in conjunction with a calomel (saturated KCl solution used) and platinum electrode system. Instructions are followed for the specific meter to obtain MV readings. E_h is measured by inserting the electrodes just into the surface of the undisturbed sediment (about 1/2").

The oxidation-reduction potential of the sample in millivolts referred to the hydrogen scale is calculated as follows:

Oxidation-reduction potential, $Mv = E - C$ where:

E = electromotive force, in millivolts of the cell

C = potential, in millivolts of the saturated calomel electrode referred to the hydrogen scale.

Note: There should not be any electrical interferences in the immediate locale.

Reference

Manual on Industrial Water, Second Ed., 1966 Printing,
No. 148-1, pages 578-582.